SOME PLATINUM SUBSTITUTED SILYL AND GERMYL COMPOUNDS

by

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TO MY PARENTS

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SUMMARY.

The introduction is a review of two aspects of silicon and germanium transition metal chemistry. Silicon and germanium hydride compounds are considered first, followed by platinum derivatives of organosilanes and germanes.

Some silyl and germyl platinum compounds trans-$XPt(PEt_3)_2MH_{(3-n)}Y_n$ (n = O to 3; M = Si, Ge; X, Y = Cl, Br, I) have been prepared by reaction of silyl and germyl compounds $MH_{(4-n)}Y_n$ with platinum hydrides trans-$XPt(PEt_3)_2H$. When X differs from Y there is halogen exchange leading to that product with the heavier halogen bound to platinum. The proton n.m.r. and vibrational spectra of these compounds are discussed and a mechanism for the preparative reaction involving oxidative addition of M-H followed by elimination of H_2 is postulated.

Oxidative addition of XH_2M-H to trans-$IPt(PEt_3)_2I$ gives $I_2Pt(PEt_3)_2H$. MH_2X which decomposes slowly and gives eventually trans-$IPt(PEt_3)_2MHXI$ and H_2. The same six-coordinated compounds are formed by addition of HI to trans-$IPt(PEt_3)_2MH_2X$. Similar reactions have been investigated for SiH_4, GeH_4 and with Cl substituted for I at Pt. The compounds trans-$ClPd(PEt_3)_2SiH_2Cl$ and trans-$ClPd(PEt_3)_2SiHCl_2$ are formed by treatment of trans-$ClPd(PEt_3)_2Cl$ with SiH_3Cl.

The reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$(I) with Me_2NH gives trans-$ClPt(PEt_3)_2SiH_2NMe_2$. The reactions of (I) with

MeOH, Et_3P, water, MeI, Me_3N, C_2H_4 and PH_3 have been studied.

Digermane, disilane and its derivatives when treated with trans-$XPt(PEt_3)_2H$ form disilyl and digermyl platinum compounds; SiH_3SiH_2Cl forms trans-$IPt(PEt_3)_2SiHCl.SiH_3$ but $SiH_3.SiHCl_2$ forms trans-$IPt(PEt_3)_2SiH_2.SiHCl_2$.

Tris(germyl)bis(phosphine) platinum hydrides are formed by treatment of trans-$ClPt(PEt_3)_2GeH_2Cl$ with excess GeH_3Cl and have been studied by H^1 n.m.r. A similar tris(germyl) compound is formed by treatment of (I) with GeH_3Cl. A concurrent silyl/germyl exchange leads to SiH_3Cl and trans-$ClPt(PEt_3)_2GeH_2Cl$.

The mechanisms of many of these reactions have been interpreted in terms of six-coordinated intermediates.

CONTENTS

INTRODUCTION

There has been much interest, during the last few years, in the chemistry of transition metal derivatives of silicon and germanium[1,2]. This has been due, in part, to the possible relationship between these compounds and intermediates involved in the industrially important hydrosilation of olefins[3]. Most of the work has been concerned with organo-silyl and germyl derivatives, however, and only a few workers have investigated the parent hydride compounds. The work in this thesis deals with the preparation and properties of silicon and germanium hydride derivatives of platinum, and the introduction presents a brief review of the relevant chemistry in this field. The review includes some chemistry which was reported after commencement of the work described in the thesis. It is considered from two aspects: the chemistry of the hydride group when coordinated to a transition metal, and the chemistry of the silicon-platinum and germanium-platinum bonds.

The first report of a silicon hydride transition metal complex was by Aylett in 1965[4], when he prepared silyltetracarbonylcobalt, by treating the sodium salt of cobalt tetracarbonyl anion with iodosilane. The same reaction was used to prepare silyene-bis(tetracarbonylcobalt)[5]:

$$SiH_{4-x}I_x + NaCo(CO)_4 \xrightarrow{-23^{o}} SiH_{4-x}[Co(CO)_4]_x + xNaI.$$

$SiH_3Co(CO)_4$ is a pale yellow, volatile liquid which slowly

disproportionates at room temperature to give SiH_4 and $SiH_2[Co(CO)_4]_2$ the vapour is stable at this temperature. An electron diffraction determination of the molecular structure in the gas phase indicated a trigonal bipyramid with C_{3v} symmetry[6]. In common with many silicon hydride compounds, $SiH_3Co(CO)_4$ is air sensitive. It reacted only slowly with air at reduced pressure but when a tube of vapour was smashed, " A yellow flash and mild explosion were noted." The Si-Co bond is cleaved by HF, HCl and H_2O, forming $HCo(CO)_4$, and SiH_3F with HF, SiH_3Cl with HCl and solid $(SiH_2O)x$ polymers with H_2O. Mercuric halides react rapidly and completely with $SiH_3Co(CO)_4$ vapour to form silyl halides and $Hg(Co(CO)_4)_2$. Triphenyl phosphine slowly replaces a carbonyl group from cobalt, producing a compound which is probably $H_3SiCo(CO)_3PPh_3$. Adducts are formed with tertiary amines[7] and their infrared spectra indicate that they are probably ionic and of the form: $[H_3Si2B]^+[Co(CO)_4]^-$ where B is NMe_3 and pyridine, and 2B is bipyridine. SiH_3Cl and SiH_3I form similar adducts[8,9].

Silylmanganesepentacarbonyl was prepared[10] in high yield by a reaction similar to the preparation of $SiH_3Co(CO)_4$:

$$SiH_3I + NaMn(CO)_5 \xrightarrow[\text{ether}]{-23^\circ} SiH_3Mn(CO)_5 + NaI$$

The product when pure is a volatile, colourless solid melting at 25° and is thermally more stable than $SiH_3Co(CO)_4$. The reaction of $SiH_3Mn(CO)_5$ with air was similar to that of the cobalt complex,

being slow at normal pressure, but shock induced detonation. All reactions expected to result in cleavage of the silicon-metal bond are more difficult with $SiH_3Mn(CO)_5$ than with $SiH_3Co(CO)_4$. Water reacted slowly at room temperature to form $(SiH_3)_2O$ and $HMn(CO)_5$; the reaction was 33% complete after ten minutes. Under normal conditions other reagents expected to cleave the Si-Mn bond show no reaction; however, when the liquid compound is heated with HCl it reacts in a different manner:

$$SiH_3Mn(CO)_5 + xHCl \xrightarrow{75^\circ} SiH_{3-x}Cl_xMn(CO)_5 + xH_2$$

$$x = 1 - 3.$$

This reaction is unusual because SiH_3- compounds normally require a Lewis acid as catalyst for halogenation by HCl[11]. Adducts are formed with tertiary bases in the same manner as the cobalt complex; the adducts react rapidly with HCl even at -100°:

$$SiH_3Mn(CO)_5, 2py + 3HCl \longrightarrow SiH_3Cl + HMn(CO)_5 + 2pyHCl.$$

This fast reaction contrasted with the inertness of free $SiH_3Mn(CO)_5$ towards HCl at room temperature, and lent support to the ionic structure which was indicated by the infrared spectrum.

Aylett has also prepared tetracarbonyldisilyliron[12]:

$$SiH_3I + Na_2Fe(CO)_4 \xrightarrow[\text{butane}]{20^\circ} (SiH_3)_2Fe(CO)_4 + 2NaI.$$

A small amount of hydridotetracarbonylsilyliron, $SiH_3FeH(CO_4)$,

was isolated in addition to the main product. Tetracarbonyldisilyliron is a readily sublimable white solid at room temperature and $(SiH_3)HFe(CO)_4$ is a pale yellow liquid, less thermally stable than the disilyl iron complex. Tetracarbonyldisilyliron is similar in chemical behaviour to $SiH_3Co(CO)_4$ and $SiH_3Mn(CO)_5$ and intermediate between them in reactivity; thus air at atmospheric pressure reacts violently, and hydrolysis is quite rapid with the formation of $(SiH_3)_2O$ and $H_2Fe(CO)_4$. Hydrogen chloride reacted slowly just above room temperature; 9% of the Si-Fe bonds were cleaved giving SiH_3Cl with mainly $SiH_3FeH(CO)_4$ and some $H_2Fe(CO)_4$. With NMe_3 the expected 1:4 adduct was not formed, possibly for steric reasons; only the 1:2 adduct was formed which was shown to have the symmetrical structure: $[(SiH_3B)_2]^{+2}[Fe(CO)_4]^{-2}$.

The number of germanium hydride transition metal complexes which have been studied is limited, even in comparison with the silicon hydride derivatives. This may be due to the compounds and starting materials possessing a lower thermal stability. The bond energy E(Ge-H) in GeH_4 is 68.9 kcal/mole in comparison with 76.5 kcal/mole for E(Si-H) in SiH_4[13]. Both silicon-hydrogen and germanium-hydrogen bonds are thermodynamically unstable with respect to oxidation, but in most compounds Ge-H bonds are less readily oxidized than Si-H bonds. (Oxidation of GeH_4[14] occurs on heating to between 150° and 230° depending on the conditions, but

SiH_4[15] can explode with oxygen even at -140°). This difference in reactivity may be because the Si-H bond is less thermodynamically stable than the Ge-H bond, [E(Si-O) in SiO_2 is ~112 kcal/mole in comparison with 85 kcal/mole for E(Ge-O) in GeO_2[16]] but the silicon hydrides may also be less kinetically stable. The greater resistance to oxidation of the Ge-H bond is illustrated by the fact that two of the compounds discussed below are air-stable.

Bis-(pentacarbonyl)-manganese-germane was first reported in 1963[17]; it was prepared by the action of germane on pentacarbonylmanganesehydride for eight days at room temperature.

$$GeH_4 + HMn(CO)_5 \longrightarrow H_2Ge[Mn(CO)_5]_2 + H_2.$$

It was isolated as an air-stable solid in 95% yield (based on the amount of $HMn(CO)_5$ consumed). Since no $H_3GeMn(CO)_5$ or $HGe[Mn(CO)_5]_3$ was formed, it was proposed that the mechanism might involve the formation of GeH_2.

The second germanium hydride derivative reported[18] was prepared by the reduction of bis(dicarbonyl-π-cylopentadienyliron)-bis(chloro)germane:

$$[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 + GeCl_4 \longrightarrow Cl_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 \xrightarrow{NaBH_4} H_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$$

The product, an air sensitive solid, was identified by a Ge-H stretch at 2012 cm^{-1}. It was soluble in chloroform, by which the Ge-H bonds were chlorinated after a prolonged time.

Germylpentacarbonylmanganese was prepared[19] in a reaction analagous to the preparation of $SiH_3Mn(CO)_5$:

$$H_3GeBr + NaMn(CO)_5 \longrightarrow H_3GeMn(CO)_5 + NaBr.$$

It is a volatile, colourless solid which can be distilled in a vacuum line. It differs from $H_3SiMn(CO)_5$ since it is unchanged after remaining in contact with air for a long period of time.

The germyl analogue of $SiH_3Co(CO)_4$ has been prepared[20] by an exchange reaction of GeH_3F with the silyl compound but no reactions or properties of $GeH_3Co(CO)_4$ have been reported.

The reactions of all these compounds can be divided into two broad categories:- those due to the hydride groups and those depending upon the silicon or germanium transition metal bond. The nature of this bond has been the subject of some speculation. The R_3M-group (where M is Si or Ge; R is alkyl, aryl or halogen) is essentially a σ donor, forming a σ bond with a transition metal; however, M has an unfilled d orbital of the correct symmetry for overlap with a filled d orbital on the metal. The possibility of π bonding is thus introduced[21]. Graham and his co-workers have claimed that in some manganese carbonyl complexes, R_3Si- and R_3Ge- act as good π acceptors as well as σ donors[22, 23, 24]. MacDiarmid has proposed similar properties for the R_3M group in $R_3MCo(CO)_4$[25]. Aylett's work supported the results with the manganese complexes[10], but he has cast doubt on the validity of MacDiarmid's calculations[5]. A comparison[6]

of the molecular structure for $SiH_3Co(CO)_4$[6] with that for $Cl_3SiCo(CO)_4$[26] has provided some stereochemical evidence for (d → d)π bonding in the trichloro compound. In the latter, compared with the hydride compound, the Si-Co bond is shorter and the out of plane displacement of the equatorial carbonyls is less, as expected for a stronger π acceptor. The silicon and germanium-platinum bonds have also been the subject of some discussion since Chatt reported that the methyldiphenylsilyl group on platinum had the highest inductive trans effect of any ligand known[27]. (The trans effect and theories accounting for it have been discussed by Basolo and Pearson[28]). The report was based on the assumption that the bond, trans to the ligand under consideration, was weakened by the inductive trans effect, and this was reflected in the lowering of the Pt-Cl stretching frequency in comparison with a similar compound[29]. The value of ν(Pt-Cl) for trans-$ClPt(PMe_2Ph)_2SiMePh_2$ was 242 cm^{-1} in comparison with the previous lowest recorded value of 269 cm^{-1} for trans-$ClPt(PEt_3)_2H$. The discussion was extended in a later paper[30] when some germanium and tin complexes were included. It was expected that the inductive trans effects would be in the order $Ph_3Sn > Ph_3Ge > Ph_3Si$ but the values of ν(Pt-Cl) indicated the reverse. This reverse in the order could have been caused by some π interaction between M and Pt, but when only small differences in ν(Pt-Cl) were involved the

relative values might not have been significant, due to possible coupling of the Pt-Cl vibration with other vibrations in the different molecules[31]. It was proposed that inductive trans effects might be studied, in such complexes, by observing the size of the Pt-P coupling constants in the P^{31} n.m.r. spectra. The interpretation of both the infrared and the n.m.r. data has been placed open to some doubt, because in neither case was the interpretation straightforward. Mason[32] preferred to use bond lengths as a criterion for the trans effect and found that for trans-$ClPt(PMe_2Ph)_2SiMePh_2$, the Pt-Cl bond length was 2.45 Å, the longest known in compounds of that type. He has also made a qualitative correlation, for trans-$XPt(PR_3)_2Y$, between bond length and difference in M-Y and M-X σ overlap integrals. The difference was a maximum when Y was silicon or hydrogen. The trans effect has been studied by observing the rate of replacement of Cl^- by pyridine in trans-$XPt(PR_3)_2Cl$[33], and the high trans effect of R_3Si- was confirmed when it was found that the rate of a similar reaction when X = R_3Si-, was too fast to measure[30]. In the chemistry of M-Pt complexes,which is described later, the trans effect appears to play an important part in some reactions where breaking of a platinum-ligand bond is involved.

Nearly all alkyl, aryl, silyl and germyl platinum compounds, which have been prepared, contain ligands such as R_3P or R_3As coordinated to platinum. The order of stability for such

complexes in one Group VIII triad is Pt > Pd > Ni. Using Molecular Orbital Theory, Chatt and Shaw have offered a qualitative explanation for this behaviour in alkyl complexes[34]. With some extension the same explanation probably applies to silyl and germyl compounds. They have assumed that the mechanism for decomposition of the R-Pt bond occurs by promotion of an electron from the highest filled (π) orbital into the lowest unfilled orbital, which is the R-Pt σ anti-bonding orbital. Ligands with orbitals of π symmetry (such as R_3P, R_3As) when coordinated to platinum may interact with the highest filled (π) orbital and lower its energy, thereby enhancing the kinetic stability of the complex. Since the difference between the energies of the π and σ molecular orbitals (ΔE) increases from Ni to Pt the theory predicts that the kinetic stabilities of complexes will be in the order Pt > Pd > Ni. If any π bonding is possible between R and Pt[35] (which may be the case when M is Si or Ge), it is proposed that the M-Pt bond will be more stable, partly because of the extra M-Pt interaction, and partly due to a further increase in ΔE.

Formation of the M-Pt (M = Si, Ge) bond has been achieved by several methods. The first report was in a communication by Glockling[36] in 1964, and he has since published a paper describing the reaction[37]:

cis or trans-$(Et_3P)_2PtCl_2 + 2Ph_3GeLi \rightarrow (Et_3P)_2Pt(GePh_3)_2 + 2LiCl$.

The reaction probably took place in two stages, but it was not found possible to isolate a mono-germyl species, presumably because the second substitution reaction was faster than the first, perhaps due to the trans effect of Ph_3Ge-. The reaction has been extended by Chatt to include some bis($MePh_2Si$-) and some bis(Me_2PhSi)-platinum compounds[30]. When the starting material $(Et_3P)_2PtI_2$ was used, the reaction was found to be complicated by the formation of Li-Pt bonds. On hydrolysis of the reaction mixture a series of compounds including Ph_6Ge_2, $IPt(PEt_3)_2H$, $(Et_3P)_2PtH.GePh_3$, $(Et_3P)_2Pt.OH.GePh_3$ and $(Et_3P)_2Pt(GePh_3)_2$ were isolated[37]. This hydrolysis reaction perhaps explains the formation of $(Et_3P)_2Pt.H.SiPh_3$ in the reaction of Ph_3SiLi with $(Et_3P)_2PtCl_2$, reported by Baird[38]. The complexes $(R_3P)_2Pt(MR'_3)_2$ were found to be sometimes cis, sometimes trans and sometimes a mixture of both in solution. The stereochemistry was studied using infrared[39], n.m.r.[31,40], and dipole moment[41] techniques.

In order to minimise the difficulties due to solubility and to simplify the spectroscopic properties, it was considered desirable to prepare the trimethylsilyl and trimethylgermyl derivatives. Glockling has developed a method for preparing these derivatives using $(Me_3M)_2Hg$[42,43] instead of the lithium compounds Me_3SiLi and Me_3GeLi which were unknown:

$$(Me_3M)_2Hg + cis(Et_3P)_2PtCl_2 \xrightarrow[reflux]{C_6H_6} trans\ ClPt(PEt_3)_2MMe_3 + Hg + Me_3MCl$$

The stereochemistry of the product was assigned from the n.m.r. spectrum. In contrast to the previous preparative method it was not found possible to prepare bis-(MMe_3)-Pt derivatives. The Me_3M-group has an extremely high trans effect, greater than Ph_3M-, possibly due to the additional inductive effect of the methyl groups. It was therefore suggested[41], that the bis-(Me_3M)-Pt complex was inherently unstable, and in confirmation of this view, $HPt(PEt_3)_2GeMe_3$ was only 'marginally stable'.

Another method for producing platinum silicon bonds was by reaction of silicon hydrides with platinum(O) compounds[44]:

$$R_3SiH + Pt(PPh_3)_4 \longrightarrow (PPh_3)_2PtH.SiR_3 + 2PPh_3 \quad - (1)$$

$$2R_3SiH + Pt(PPh_3)_4 \longrightarrow (PPh_3)_2Pt(SiR_3)_2 + H_2 + 2PPh_3 \quad - (2)$$

where R_3Si is Cl_3Si, Ph_2HSi, $(m\text{-}F.C_6H_4)_3Si$, $(m\text{-}CF_3,C_6H_4)_3Si$ and $(p\text{-}CF_3C_6H_4)_3Si$. Whether the reaction followed the course indicated by (1) or (2) depended on the nature of R and the conditions of the reaction. A similar series of reactions was observed for $Pt(disphos)_2$. (diphos = $Ph_2P.CH_2.CH_2P.Ph_2$). When $(diphos)PtH.SiCl_3$ was refluxed in benzene a compound was formed which had a formula consistent with $[Pt(SiCl_2)(diphos)]$, and which could have been a dimer with two $SiCl_2$ bridges

between the platinum atoms.

A similar reaction in which a silicon-silicon bond was added across Pt(O) has been reported[45]:

$$Si_2Cl_6 + Pt(Ph_3)_4 \longrightarrow (PPh_3)_2Pt(SiCl_3)_2 + 2PPh_3.$$

When some organosilanes were reacted[30] with cis-$(QMe_2Ph)_2PtX_2$ (X is Cl, Br; Q is As, P) in benzene/triethylamine, HX was removed by the base and platinum silyl compounds were formed:

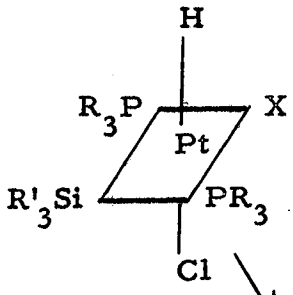
$$R_3SiH + cis\text{-}(QMe_2Ph)PtCl_2 + Et_3N \longrightarrow trans\text{-}ClPt(QMe_2Ph)_2SiR_3 + Et_3NHCl$$

Similar products were formed when silicon and germanium hydrides were reacted with hydridochloro-complexes of platinum(II)[30,46]:

$$R_3MH + trans\text{-}ClPt(PR_3)_2H \longrightarrow trans\text{-}ClPt(PR_3)_2MR_3 + H_2.$$

The reaction appeared to be assisted by the presence of electron withdrawing groups on M.

The last two reactions were not only similar in the products that they yielded, they were also thought to proceed via the same mechanism. It was postulated that platinum(II) was converted into a six-coordinated platinumIV intermediate by oxidative addition of the R_3Si-H bond across Pt, and the final product formed by elimination of two ligands.

$R'_3SiH + (PR_3)_2PtClX \longrightarrow$ 

(X = Cl, H)

$ClPt(PR_3)_2SiR'_3 + HX.$

H_2 was removed as hydrogen gas and HCl was removed as Et_3NHCl. Removal of H_2 was necessary because this reaction was found to be reversible.

The reaction between hydrogen and a platinum germyl compound was first studied by Glockling[36,37], using $(PEt_3)_2Pt(GePh_3)_2$ under very mild conditions:

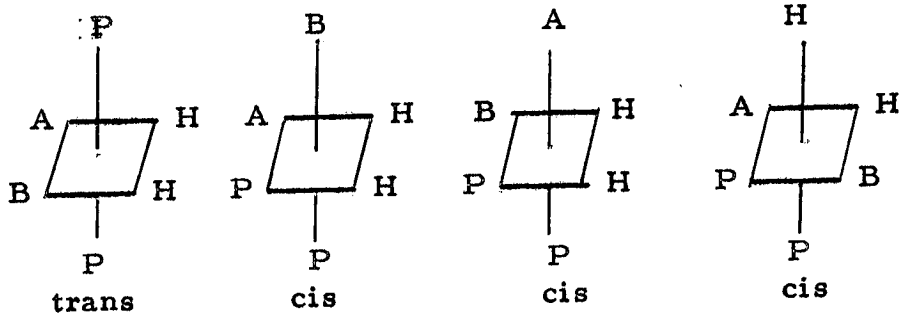
$$H_2 + (PEt_3)_2Pt(GePh_3)_2 \xrightarrow[1\ \text{atmos.}]{\text{room temp}} (PEt_3)_2PtH.GePh_3 + Ph_3GeH.$$

The reaction was not quite quantitative. From rate determinations made at 0° and 25° the activation energy was estimated to be about 9kcal. This very low value explains the reason for the reaction occurring under such mild conditions, and together with the nature of the products suggests an addition-elimination mechanism. The R_3M-Pt bond was broken more easily when R was Me than when R was Ph, and a reaction in which both Me_3M- and Ph_3M- were coordinated to platinum was extremely selective[43]:

$$trans\text{-}Me_3GePt(PEt_3)_2GePh_3 + H_2 \longrightarrow trans\text{-}HPt(PEt_3)_2GePh_3 + HGeMe_3$$

The trans complexes are more labile towards hydrogen, than the

cis complexes, the latter requiring H_2 at 100 atmospheres and 20° to break the M-Pt bond. This was explained by consideration of the possible intermediates, assuming cis addition of hydrogen followed by cis elimination, and that the phosphines retained their original positions.



(P = R_3P)

$$APt(PR_3)_2B + H_2 \longrightarrow APt(PR_3)_2H + HB$$

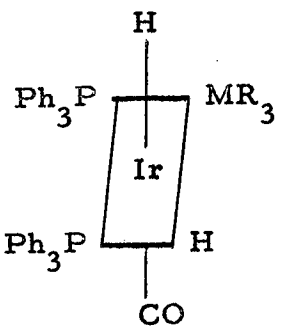
The first intermediate was considered likely to be the most labile because it was the only structure in which both leaving ligands were opposite to groups of high trans effect. The assumption of cis addition and elimination has some justification apart from the low activation energy. Vaska has prepared[47] an isoelectronic iridium(I) compound which adds hydrogen reversibly in a cis configuration[48].

$$(PPh_3)_2Ir.CO.Cl + H_2 \longrightarrow cis\text{-}(PPh_3)_2IrH_2.CO.Cl.$$

The preparative reactions, which occur by addition of the R_3M-H bond to Pt, also have some parallels in iridium chemistry. The first report of a similar reaction was reversible addition of Cl_3Si-H and $(EtO)_3SiH$ to $(PPh_3)_2Ir.CO.Cl$ forming a six-coordinate adduct[49]. The work was investigated further[50, 51]

and it appeared that this was the first stage in a two-stage reaction.

$$(PPh_3)_2Ir.CO.Cl + R_3MH \longrightarrow (PPh_3)_2IrH.CO.Cl.MR_3$$



$$(PPh_3)_2IrH.CO + R_3MCl \xleftarrow{R_3MH}$$

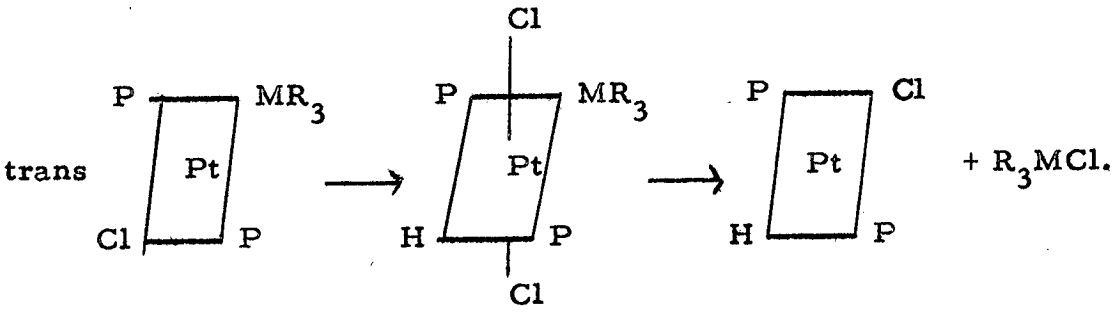
The stereochemistry of the final product, which was probably formed by cis addition of R_3M-H to the iridium hydride, was determined by infrared and n.m.r. studies.

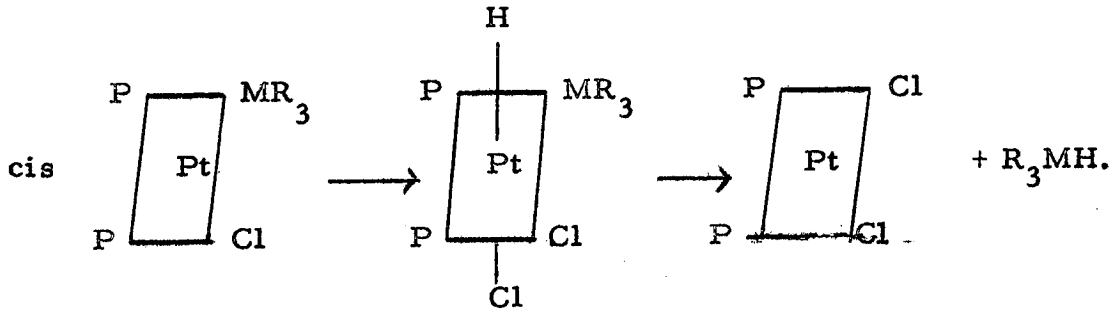
Six-coordinated platinum hydrides have been formed by addition of HCl to trans-$ClPt(PR_3)_2H$ [52] and to $Pt(Ph_3P)_4$ [53]. The rate of cleavage of a phenyl group by HCl from trans $PhPt(PEt_3)_2Ph$ has also been interpretated in terms of a six-coordinated intermediate [54]. The assumption that HCl reacts similarly with R_3M- derivatives of platinum has made it possible to offer an explanation of some unusual reactions.

$$HCl + ClPt(PR_3)_2MR'_3 \longrightarrow ClPt(PR_3)_2H + R'_3MCl$$

The reaction [46] was quantitative and R'_3MCl was probably produced by elimination from an intermediate: $Cl_2PtH(PR_3)_2.MR'_3$. When HCl was reacted with trans-$R_3MPt(PEt_3)_2MR_3$, the reaction proceeded in two stages forming at first trans-$ClPt(PEt_3)_2MR_3$

and R_3MH and then trans-$ClPt(PEt_3)_2H$ and R_3MCl[30, 37]. With a cis platinum complex, however, the final products were cis-$(PR_3)_2PtCl_2$ and $2R_3MH$. This difference can be understood by consideration of the possible intermediates involved in the second stage of the reaction:

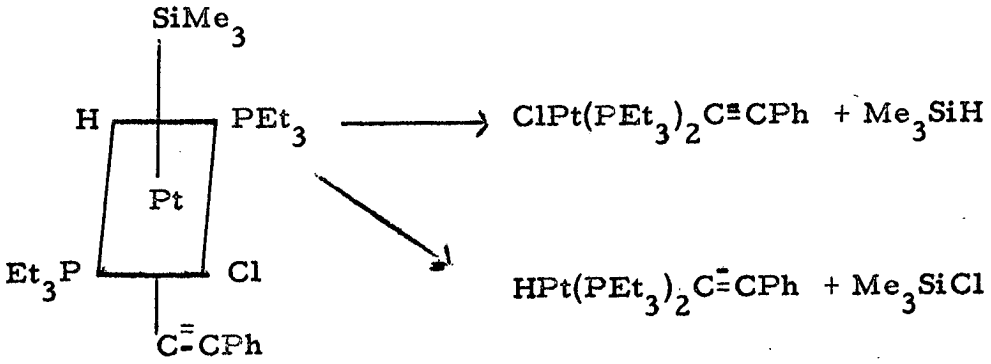




It was assumed that R_3MH was eliminated preferentially, but in the reaction with the trans isomer, it was only possible to eliminate R_3MCl, because of the stereochemistry of the intermediate. As in the hydrogenolysis reaction, when two different groups such as Ph_3Ge- and Me_3Ge- were joined to platinum, the first stage of the reaction selectively removed Me_3GeH. [with a little (2%) Me_3GeCl].

In the reactions discussed above the postulated intermediates decomposed cleanly with the formation of only two products. The reaction of phenyl acetylene with trans-$ClPt(PEt_3)SiMe_3$ was

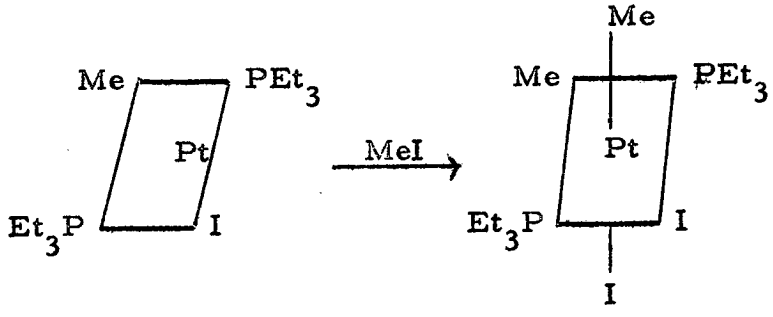
explained by postulating two modes of elimination from a six coordinated intermediate[43].



Several minor products were also detected. With trans-$ClPt(PPh_3)_2SiPh_3$ Ph.C≡CH reacted differently and inserted into the Si-Pt bond forming $ClPt(PPh_3)_2C_2H.Ph.SiPh_3$[55]. Insufficient evidence was obtained to enable discussion of any mechanism.

The reactions of silyl and germyl platinum compounds with Cl_2, Br_2, I_2, MgI_2, MeI, Cl_3SiH and Me_3GeH[30, 37, 44, 56] were interpretated in terms of Pt(IV) intermediates, but as in all the examples discussed above, no definite evidence for any isolated intermediate was presented. However, other platinum compounds were known to form adducts with halogens[35], MgI_2[34] and MeI[34]:

e.g.



Some six coordinated trichlorogermyl compounds such as $(Ph_3P)_2PtCl_3GeCl_3$ are known[62].

Cleavage of the M-Pt bond was also observed in two reactions which did not involve six coordinated intermediates. The compounds were hydrolysed in aqueous diglyme[43];

$$2ClPt(PR_3)_2MMe_3 + H_2O \longrightarrow 2ClPt(PR_3)_2H + (Me_3M)_2O.$$

When M was Si the hydrolysis occurred immediately but when M was Ge, the reaction was only half completed after 215 hours at 18°. This suggests that the reaction occurs with nucleophilic attack by water at silicon, as it is similar to the rapid base hydrolysis of organosilanes in comparison with the slow hydrolysis of organogermanes[58]. The M-Pt bond was broken in a reaction with ethylene dibromide,[37] in a reaction which appeared to be a general property of germanium transition metal bonds[57,59].

$$(PR_3)_2Pt(GePh_3)_2 + C_2H_4Br_2 \rightarrow 2Ph_3GeBr + (PR_3)_2PtBr_2 + C_2H_4$$

When $(diphos)Pt(SiHPh_2)_2$ was treated with an equimolar amount of bromine[44], Br was substituted for H at silicon without breaking the Si-Pt bond. The product reacted further on treatment with MeLi.

$$(diphos)Pt(SiHPh_2)_2 \xrightarrow{Br_2} (diphos)Pt(SiBrPh_2)_2 \xrightarrow{LiMe} (diphos)Pt(SiMePh_2)_2$$

All other reactions reported involved the other ligands coordinated to platinum. The Cl^- ion has been replaced in a series of reactions[43,55], the ease of which could be related to the high trans effect of Si and Ge:

$ClPt(PR_3)_2MR'_3 + NX \longrightarrow NCl + XPt(PR_3)_2MR'_3$.

(N is Na, K, Li; X is Br, I, CN, NCS, N_3, Ph, $GePh_3$).

$InCl_2$ and $SnCl_2$ inserted into the Pt-Cl bond giving - Pt -$InCl_3$ and -Pt $SnCl_3$ complexes[55].

The phosphine ligands have been replaced by diphos, the mono and bis substituted compounds reacting in different ways[30,46]:

$diphos + Pt(PR_3)_2(MR'_3)_2 \longrightarrow Pt(diphos)(MR_3)_2 + 2R_3P$

$diphos + ClPt(PR_3)_2MR'_3 \longrightarrow [diphos\ PtPR_3.MR'_3]^+Cl^- + R_3P$

The salt reacted in rather an unusual way. In benzene solution with HCl it formed a white precipitate, at first thought to be the six coordinated adduct[46], but further investigation indicated: $[(diphos)PtPEt_3.GeMe_3]^+HCl_2^-$ [60]. The reaction of water with $[(diphos)PtPR_3SiMe_3]^+Cl^-$ was very slow in comparison with $ClPt(PR_3)_2SiMe_3$. This was attributed to the positive charge directing attack by water onto Pt, in comparison with attack at Si in the neutral compound.

The platinum complexes, which have been discussed, are mostly thermally quite stable. They can, in some cases, be heated to 100° without decomposition and are able to exist unchanged in solution at room temperature for long periods. In contrast to this, the only palladium derivatives which have been made are compounds such as $(PEt_3)_2Pd(GePh_3)_2$[59]. They are very much less stable and decompose in toluene even at -20°.

This has made their chemistry more difficult to study, but apart from the lack of any evidence for six-coordinated intermediates, it appears to be similar to that of the analagous Pt compounds.

Nickel compounds are expected to be even less stable and only two have been prepared: $\pi C_5H_5.CO.NiSiCl_3$, by reaction of $SiCl_3H$ with $[\pi C_5H_5(CO)Ni]_2$[23], and $[Ph_3SiNi(CO)_3]^-$ by reaction of $LiSiPh_3$ with $Ni(CO)_4$[61].

A large number of the compounds discussed above were identified, and their stereochemistry assigned using spectroscopic methods[31,39,40]. In some cases in order to simplify the assignments[42] it was considered desirable to prepare the trimethylsilyl and trimethylgermyl platinum compounds, which had the least complicated spectra. A study of the parent hydride compounds offers further advantages. The infrared spectra have characteristic M-H modes of vibration which are well separated from modes due to carbon-hydrogen. The main advantage, however, is that in the n.m.r. spectra the proton resonance of H-M is more sensitive to the nature of the transition metal and its substituents. There is, in organo compounds, at least one more bond between the nearest proton to M and the transition metal. This suggests that silicon and germanium hydride transition metal compounds might be more easily identified by their infrared and n.m.r. spectra, than organo derivatives.

CHAPTER I

THE PREPARATION AND SPECTROSCOPIC PROPERTIES OF SOME FOUR-COORDINATED PLATINUM SILYL AND GERMYL COMPOUNDS

1.1 The Preparative Reaction

Silicon-platinum and germanium-platinum compounds have been prepared by the reaction of tris(organo)- and tris(halo)- silicon and germanium hydrides with hydrido-platinum compounds[30, 63], as described in the introduction. The reaction can be used as a very convenient method for the preparation of silicon and germanium hydride derivatives of platinum. Silyl halides, SiH_3X, react smoothly with an equimolar amount of trans-$XPt(PEt_3)_2H$ at room temperature in benzene. Hydrogen is evolved and monohalosilylplatinum complexes are formed:[86, 89]

$$\text{trans-}XPt(PEt_3)_2H + SiH_3X \longrightarrow \text{trans-}XPt(PEt_3)_2SiH_2X + H_2$$

$$X = Cl, Br, I.$$

The reaction is complete after about five minutes, but when X = Cl a low temperature n.m.r. experiment showed that the reaction was slow at -60°. The amount of hydrogen evolved in each reaction can be measured using a Toepler pump and is quantitative provided that the silane is not taken in excess. The stereochemistry of the products can easily be determined by consideration of the n.m.r. spectra, which show that both

phosphorous atoms are apparently equivalent with respect to the silyl group, which is hence trans to X. The n.m.r. spectra are discussed further in section 1.4. The products have been isolated as white or palé yellow crystalline solids by evaporation of the solvent; they have been characterised by their infrared, Raman and n.m.r. spectra, and (in some cases) by analysis.

The solids are stable under vacuum for several weeks, but in solution in benzene they are rather less stable, sometimes decomposing after a few days with the formation of a yellow solid which changes into a brown tar. They are also very moisture-sensitive and can only be handled under vacuum or in a dry inert atmosphere.

Di- and trihalosilanes react with platinum hydrides to give analogous products:

$$\text{trans-XPt(PEt}_3)_2\text{H} \begin{cases} \xrightarrow{\text{SiH}_2\text{X}_2} \text{trans-XPt(PEt}_3)_2\text{SiHX}_2 + \text{H}_2 \\ \xrightarrow{\text{SiHCl}_3} \text{trans-XPt(PEt}_3)_2\text{SiCl}_3 + \text{H}_2 \end{cases}$$

The reaction with SiH_2X_2 proceeds at a similar rate to the reaction with SiH_3Cl, but $SiHCl_3$ reacts more slowly, not quite reacting fully after one day (indicated by the measured volume of hydrogen evolved). Platinum substituted silyl halides containing Si-H bonds do not react further with platinum hydrides; there is no reaction after several hours:

$$\text{trans-XPt(PEt}_3)_2\text{SiH}_2\text{X} + \text{trans-XPt(PEt}_3)_2\text{H} \longrightarrow \text{bis[XPt(PEt}_3)_2]\text{SiHX} + \text{H}_2$$

Mono- and dihalogermanes react in the same way as the analogous silanes with an equimolar amount of trans-$XPt(PEt_3)_2H$, but the products are less thermally stable. The least stable of them, trans-$IPt(PEt_3)_2GeH_2I$, decomposes in solution after about fifteen minutes and the most stable of them, trans-$ClPt(PEt_3)_2GeH_2Cl$ decomposes after about one hour; the solutions initially colourless, turn dark brown. The products can not be isolated as solids by evaporating the solvent at room temperature because they decompose, leaving a dark brown tar; however, by careful evaporation of the solvent at -22°, the most stable product, trans-$ClPt(PEt_3)_2GeH_2Cl$, was isolated as a pale yellow solid. It was characterised by its infrared and n.m.r. spectrum and by analysis. The other products have only been identified by their spectroscopic properties in solution.

Monosilane and monogermane react much more slowly with the platinum hydrides, but the n.m.r. spectra of the resulting solutions indicate that the reactions proceed in a similar manner to the silyl and germyl halides:

$$MH_4 + \text{trans-}XPt(PEt_3)_2H \longrightarrow \text{trans-}XPt(PEt_3)_2MH_3 + H_2.$$

The reaction of SiH_4 with trans $ClPt(PEt_3)_2H$ at room temperature is incomplete even after one week; after which the solution turns dark brown and the product decomposes. With trans-$BrPt(PEt_3)_2H$ and trans-$IPt(PEt_3)_2H$, the reaction

is faster and goes to completion (determined by hydrogen evolution) in two days, after which the products can be isolated as pale yellow solids by evaporation of the solvent; they have been characterised spectroscopically and by analysis. The reaction with monogermane is faster than with silane, being complete after about one hour, but the products are thermally unstable and have only been identified by their spectroscopic properties in solution.

1.2 Halogen Exchange

When the halogen bound to M in MH_3X differs from the halogen bound to platinum in $YPt(PEt_3)_2H$, the resulting reaction is accompanied by halogen exchange, leading to the formation of the product in which the heavier halogen is bound to platinum whatever the initial halogen distribution, e.g.

$$\text{trans-ClPt}(PEt_3)_2H + MH_3Br \rightarrow \text{trans-BrPt}(PEt_3)_2MH_2Cl + H_2$$

$$\text{trans-BrPt}(PEt_3)_2H + MH_3Cl \rightarrow \text{trans-BrPt}(PEt_3)_2MH_2Cl + H_2$$

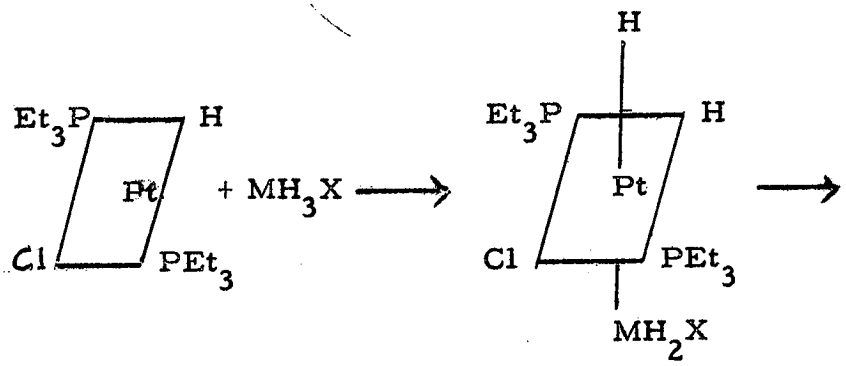
The n.m.r. spectrum of a mixture of silyl bromide and trans-$ClPt(PEt_3)_2H$ showedthat at -60° in toluene all the silyl bromide was converted into silyl chloride before the formation of any platinum-silyl compound. The platinum-silyl compound trans-$BrPt(PEt_3)_2SiH_2Cl$ was formed slowly on warming the reaction mixture to -40°. This difference in rates of reaction suggests that the mechanism of halogen exchange is different

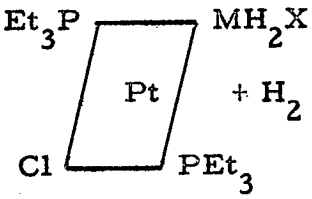
from the mechanism of formation of the platinum-silicon bond. The mechanism of the halogen exchange may be bimolecular, attack of halogen taking place at platinum or silicon. The facility with which the reaction occurs, even at -60°, indicates a low activation energy which may be due, in part, to the strong trans labilising effect on the platinum halogen of the hydrogen bound to platinum. The exchange involving transfer of light halogen to M and heavy halogen to platinum will also be energetically favourable. There is no definite data concerning the bond energy of Pt-X in related platinum halogen compounds but it appears from consideration of stability constants[64] and other data[65] that the bond energies for platinum-chlorine, platinum-bromine and platinum-iodine are either very much alike or are in the order E(Pt-I)>E(Pt-Br)>E(Pt-Cl). The bond energies of the M-X bond, however, are such that the lighter halogen bound to M is strongly favoured. This difference is illustrated in the table below, where some values for the bond energies in MX_4 are quoted[16]. They are measured in kcal/mole.

M	E(MCl)	E(MBr)	E(MI)
silicon	97.2	75.6	56
germanium	81	66	51

1.3 The mechanism of the preparative reaction

The Pt-M bond is probably formed by oxidative addition of a M-H bond to Pt(II) giving a six-coordinated Pt(IV) intermediate, which can then lose H_2 to form the four-coordinated Pt(II) product.





There is no direct evidence for such intermediates formed in reactions with platinum hydrides, even at -60°, and if they are formed they must decompose fast. The reaction is apparently reversible however, because treatment of $ClPt(PEt_3)_2D$ with SiH_3Cl leads to some incorporation of deuterium bound to silicon, presumably via formation of HD. The postulated mechanism is quite compatible with a reversible reaction, the intermediate being formed by addition of Si-H or H-H. Six-coordinated intermediates have been proposed by other workers, though none have been isolated; they have been discussed in the introduction. The isolation of such a species,

formed by analogous addition of a M-H bond to four-coordinated Pt(II) is described in Chapter II.

It is interesting to speculate on the reasons for the differing rates of reactions of a platinum hydride with the silyl compounds: $SiH_4 < SiH_3Cl \sim SiH_2Cl_2 > SiHCl_3$. It has been reported[30] that the reaction appears to be assisted by electron withdrawing groups on Si. If the rate determining step of the reaction is electrophilic attack by silicon or hydrogen at platinum, electron withdrawal from silicon would enhance such an attack. This hypothesis could account for reaction with SiH_3Cl being faster than reaction with SiH_4, but does not explain the slow reaction of $SiHCl_3$. The attack of $SiHCl_3$ may be sterically hindered, thus increasing the activation energy and reducing the rate of reaction. Support for this explanation involving the opposing effects of electron withdrawal and steric hindrance comes in the reactions of halogenated disilanes discussed in Chapter IV. The effect of different halogens (X) on the rate of reaction of silyl halides with trans-$XPt(PEt_3)_2X$ is discussed in Chapter II in terms of electrophilic attack at platinum.

1.4 H^1 n.m.r. spectra

The proton resonance spectra were recorded in benzene or (in some cases) in deuterobenzene or toluene. The general features of the spectra are now discussed. The spectrum

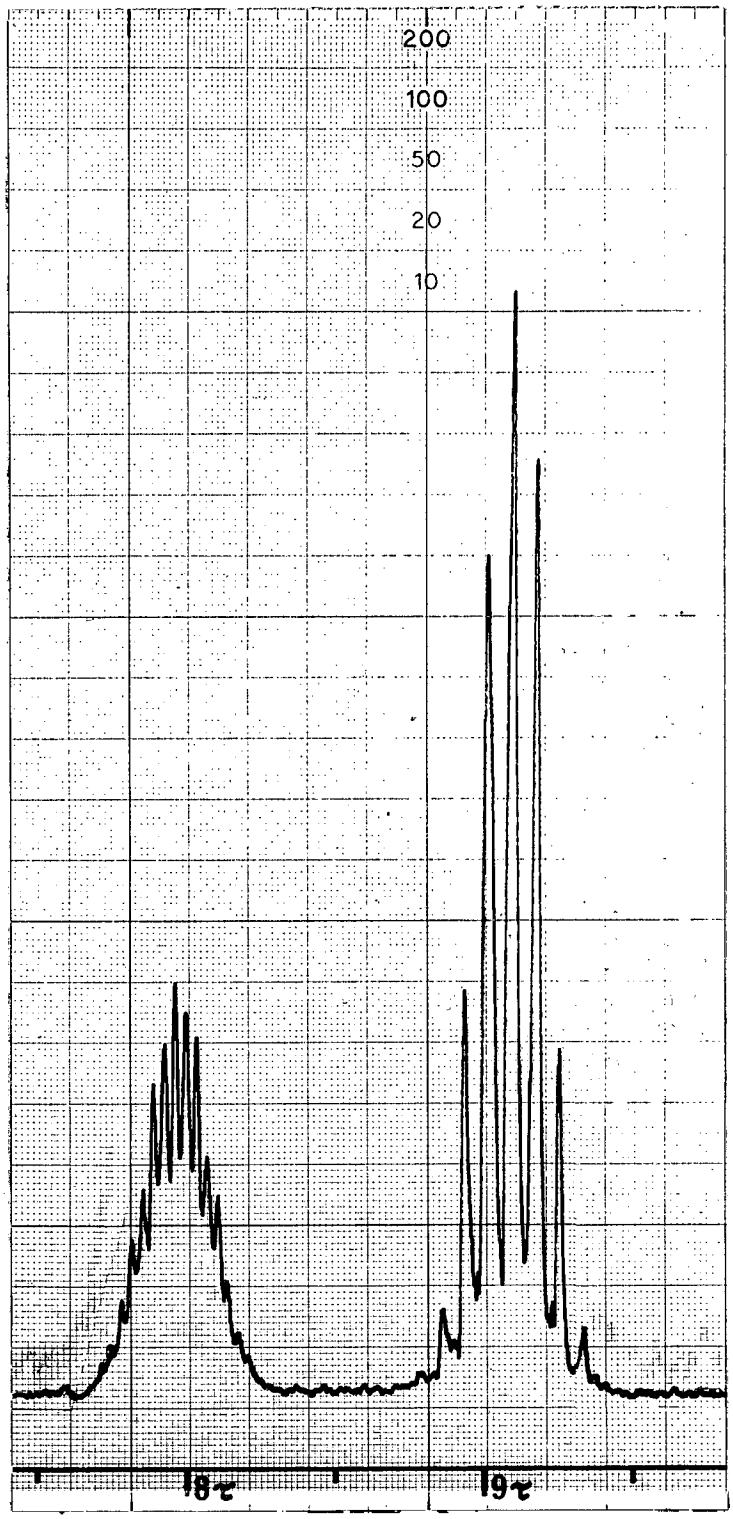


Figure 1.1

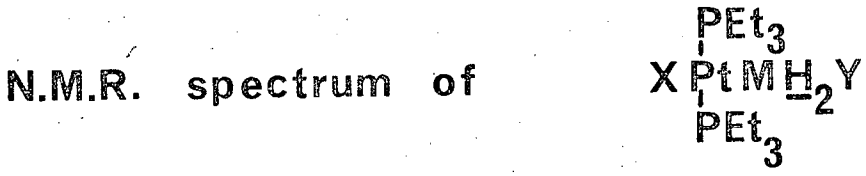
An example of a proton n.m.r. spectrum of trans-$XPt(PEt_3)_2MH_2Y$ in the region associated with Et_3P.

associated with the triethylphosphine groups is complicated and has only been used for "fingerprinting": a typical spectrum is shown in Figure 1.1. There is a "hand" of five lines at about 9T due to the CH_3- protons and a more complicated set of peaks due to -CH_2- protons at lower field. The separation of these resonances varies between O.7 and 1.3 p.p.m. according to the nature of the other ligands joined to platinum. The pattern of the resonances is typical for square planar platinum compounds with mutually trans triethylphosphine ligands[66].

The M<u>H</u> resonance is very characteristic; an example is shown in Figure 1.2. It is symmetrical and consists of three triplets with intensities in the ratio 1:4:1; the triplet splitting in each peak is due to coupling of MH with the two equivalent phosphorous atoms, and the satellites each side of the main resonance are caused by coupling with Pt^{195} for which $I = \frac{1}{2}$ and which is in 33.8% natural abundance. Thus there are three n.m.r. parameters associated with the M-H resonance of each compound: chemical shift, J(<u>H</u>M<u>Pt</u>) and J(<u>H</u>MPt<u>P</u>). These parameters are recorded in Table 1.1 for the platinum silyl compounds and in Table 1.2 for the platinum germyl compounds. The chemical shift of MH in trans-$XPt(PEt_3)_2MH_2Y$ depends on the nature of the halogen bound to M(Y) and is almost independent of the halogen bound to

Figure 1.2

N.M.R. spectrum of



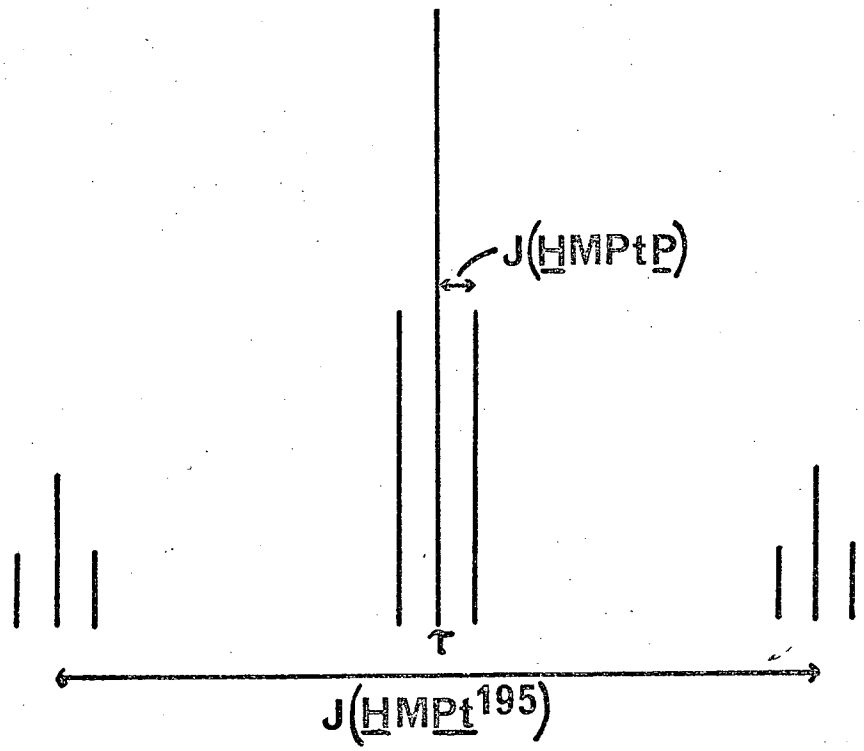


Table 1.1

Parameters from the HSi proton resonance spectra of trans-$XPt(PEt_3)_2Z$, measured for benzene solutions at room temperature relative to benzene (τ = 2.84) unless otherwise stated. The solutions were approximately 0.04 M.

X	Z	τ(HSi), ppm.	J(HSiPt)Hz.	J(HSiPtP)Hz
Cl	SiH_3	6.78[a]	28.8[a]	6.0[a]
Br	SiH_3	6.68	34.2	ca. 5.5
I	SiH_3	6.60	36.5	6.5
Cl	SiH_2F	4.11[b]	123.6[b]	5.0[b,c]
Cl	SiH_2Cl	5.37	117.6	8.8
Br	SiH_2Cl	5.29	122.7	9.3
I	SiH_2Cl	5.41	123.8	9.6
Br	SiH_2Br	5.74	127.5	9.4
I	SiH_2Br	5.65	129.2	9.7
I	SiH_2I	6.51	127.1	9.6
Cl	$SiHCl_2$	4.01	245.0	10.4
I	$SiHCl_2$	4.01	251.4	11.6
I	$SiHI_2$	4.92	213.5	12.7

(a) measured in toluene at 0^o. (b) measured in toluene at -40^o.

(c) J(HSiF) = 52.2 Hz.

Table 1.2

Parameters from the HGe proton resonance of trans-$XPt(PEt_3)_2Z$, measured under the same conditions as the HSi resonances in Table 1.1.

X	Z	τ(HGe)ppm.	J(HGePt) Hz.	J(HGePtP)Hz
Cl	GeH_3	7.20	80.0	5.8
Br	GeH_3	7.10	84.6	5.9
I	GeH_3	6.92	87.8	5.9
Cl	GeH_2Cl	4.99	218	7.4
Br	GeH_2Cl	4.98	225.6	7.5
I	GeH_2Cl	4.91	227.4	7.7
Br	GeH_2Br	5.62	227.5	7.75
I	GeH_2Br	5.51	228	7.9
I	GeH_2I	6.51	221.2	8.35
Cl	$GeHCl_2$	3.07[a]	433.6[a]	7.3[a]

(a) measured in deuterobenzene.

platinum; it is in general shifted a little to low field of the value for the parent hydride resonance in benzene. The chemical shift $\tau(M\underline{H})$ varies with different halogens in the same way as the parent hydrides, decreasing in the order: $-MH_3 > -MH_2I > -MH_2Br > -MH_2Cl > -MH_2F$, and also decreasing with increasing substitution of H by X : $-MH_3 > -MH_2X > -MHX_2$. This order is consistent with shifts to lower field, due to deshielding at H, being caused by increasing electron withdrawal from M. The coupling constants $J(\underline{H}M\underline{P}t)$ and $J(\underline{H}M\underline{P}t\underline{P})$ remain fairly constant for the compounds $XPt(PEt_3)_2MH_2X$, but $J(\underline{H}M\underline{P}t)$ is much larger for germanium than for silicon, and also increases in the series $J(\underline{H}_3M\underline{P}t) < J(\underline{H}_2XM\underline{P}t) < J(\underline{H}X_2M\underline{P}t)$.

1.5 Vibrational spectra.

The infrared spectra were recorded between 4000 and 200 cm^{-1} in benzene solutions or as nujol mulls. The Raman spectra were recorded, using solid samples, between 2,500 and 100 cm^{-1}. The frequencies of the various bands, together with assignments which are in some cases tentative, are shown in Table 1.3 for the silyl compounds and Table 1.4 for the germyl compounds. The frequencies associated with internal vibrations of triethylphosphine have not been included; they remain the same for all compounds studied. The most useful vibrations for characterising the complexes are the modes involving MH, and the MX and PtX stretching modes.

Table 1.3

Frequencies from the infrared and Raman spectra of platinum silyl compounds *trans*-$XPt(PEt_3)_2Z$ in cm^{-1}. In all the spectra there are bands near 300 cm^{-1}, between 1500 cm^{-1} and 1000 cm^{-1}, and between 780 cm^{-1} and 640 cm^{-1} assigned to modes of Et_3P groups. In some spectra there is a weak band at 235 cm^{-1} which may also be a Et_3P mode.

X	Z	Conditions	ν(SiH)	δ(SiH)	ν(SiX)	ν(PtP)	ν(PtSi)	ν(PtX)
Cl	SiH_3	B	2070 s	970 w, 945 w, 915 v.s, 570 m	-	415 w, 385 w	330 w	260 s
Br	SiH_3	B	2070 s	970 w, 945 w, 912 v.s, 560 m	-	415 w, n.o.	330 w	n.o.
Br	SiH_3	R	n.s.	n.s.	-	n.s. 375 s	335 m	n.o.
I	SiH_3	B	2080 s	970 w, 945 w, 910 v.s, 560 m	-	415 w, 385 w	330 w	n.o.
Cl	SiH_2Cl	N	2110 s	980 m, 840 s, 575 s	475 v.s	420 m, 380 m	330 w	270 s
Cl	SiH_2Cl	B	2110 s	980 m, 840 s, 580 w	480 s	420 w, 375 w	330 w	265 s
Cl	SiH_2Cl	R	2126 m	980 m, 845 m, n.o.	480 w	430 w, 382 v.s	340 s	268 s
Br	SiH_2Cl	B	2110 s	980 m, 840 s, 580 w	480 s	420 w, 370 w	328 w	n.o.
Br	SiH_2Cl	R	2114 w	980 m, n.o., n.o.	490 w	435 m, 380 vs	335 s	175 m

I	SiH_2Cl	B	2115 s	975 m, 840 s, 580 w	480 s	418 m, 385 m	330 w	n.o.
I	SiH_2Cl	R	2114 w	980 m, n.o., n.o.	n.o.	430 m, 375 v.s	335 s	148 w
Br	SiH_2Br	B	2120 s	980 m, 815 s, 570 w	400 s	450 w. obs.	340 m	n.o.
I	SiH_2Br	B	2115 s	980 m, 815 s, 570 w	400 s	obs., obs.	340 s	n.o.
I	SiH_2Br	R	2136 m	980 m, n.o., n.o.	n.o.	435 m, 375 w	344 v.s	148 w
I	SiH_2I	B	2120 s	970 m, 780 s, 545 w	302 s	415 w, 384 m	326 w	n.o.
I	SiH_2I	R	2144 s	975 m, n.o., n.o.	300 v.s	n.o., 385 w	335 m	148 s
Cl	$SiHCl_2$	B	2150 s	865 s	510 s	420 w, 370 w	330 w	270 s
					495 s			
Cl	$SiCl_3$	B			535 s	430 w, 385 w	330 w	275 s
					510 s			
					500 s			

n.o = not observed; n.s. = not studied in this region; w = weak; s = strong; m = medium intensity; v = very; obs = region obscured; N = nujol mull; B = solution in benzene; R = Raman.

Table 1.4

Infrared frequencies of platinum-germyl compounds trans-$XPt(PEt_3)_2Z$, in cm^{-1}. Modes associated with Et_3P groups are observed near 3000 cm^{-1}, between 1500 cm^{-1} and 1000 cm^{-1} and between 770 cm^{-1} and 700 cm^{-1}; the spectra were recorded for benzene solutions.

X	Z	ν(GeH)	δ(GeH)	ν(GeY)	ν(PtP)	ν(PtGe)	ν(PtX)
Cl	GeH_3	1985 s	905 m, 885 m, 830 vs	-	420 w, n.o.	225 m	260 m
Br	GeH_3	1985 s	905 m, 884 m, 828 vs	-	417 w, 383 w	d	d
I	GeH_3	1990 s	905 m, 880 m, 822 vs	-	415 m, 383 w	d	d
Cl	GeH_2Cl	2005 s	905 s, obs.	347 s	418 m, 380 w	252 m	282 m
Br	GeH_2Cl	2005 s	905 s, obs.	345 s	417 m, 383 w	245 w	n.o,
I	GeH_2Cl	2005 s	904 s, obs.	347 s	415 m, 380 w	244 m	n.o.
Br	GeH_2Br	2110 s	905 s, obs.	270 s	415 m, 382 w	241 m	n.o.
I	GeH_2Br	2110 s	904 s, obs.	270 m	415 m, 383 w	242 m	n.o.
I	GeH_2I	2110 s	904 s, obs.	n.o.	415 m, 380 w	d	d

s = strong; w = weak; m = medium intensity; v = very; n.o. = not observed;

d = sample decomposed; obs = region obscured.

The assignment of bands to ν(SiH) and δ(SiH) in the spectrum of trans-$ClPt(PEt_3)_2SiH_2Cl$ was aided by comparison with the infrared spectrum of trans-$ClPt(PEt_3)_2SiD_2Cl$. The corresponding frequencies are:

	ν(SiH) cm^{-1}	δ_2(SiH)	δ_8(SiH)	δ_5(SiH)
trans-$ClPt(PEt_3)_2SiH_2Cl$	2110	980	840	575
trans-$ClPt(PEt_3)_2SiD_2Cl$	1535	obs.	614	440

The assignments of corresponding modes in the spectra of other similar silyl and germyl compounds were made by analogy. Two MH stretching modes are expected: the antisymmetric and the symmetric stretch, and since only one band is observed in the ν(MH) region, these vibrations must have similar energies. There are four possible modes of deformation for $-MH_2X$: 'scissors', 'wagging', 'twisting' and 'rocking' vibrations. They will all be infrared active since the maximum symmetry at Si is C_s. By analogy with related compounds[67], the energy of the deformations is expected to be in the order in which they are listed above, hence δ_2(MH) is the 'scissors' mode, δ_8(MH) is the 'wagging' mode, δ_5(MH) is the 'twisting' mode and the 'rocking' mode δ_7(MH) is not observed, possibly due to coupling with platinum-ligand vibrations. (The numbering of the subscripts is the same as in the vibrational modes of CH_2Cl_2, described by Herzberg[68].). A further indication that these assignments may be correct

comes from the Raman spectra, where it is expected that the 'scissors' mode would be the most intense. In agreement with this prediction of intensities, δ_2(SiH) is the only deformation mode observed in the Raman spectra. As X changes from Cl to I, the deformation modes shift to lower frequencies. A similar shift in related compounds has been attributed partly to the increase in reduced mass, and partly to electronegativity effects[67]. Only one deformation mode is observed for the germyl compounds trans-$XPt(PEt_3)_2GeH_2Y$, other modes being obscured by triethylphosphine bands.

In the spectra of the unsubstituted species trans-$XPt(PEt_3)_2MH_3$ the three stretching frequencies expected, again coincide. The isolated $-MH_3$ group with C_{3v} symmetry has three modes of deformation: an antisymmetric bend (e), a symmetric bend (a_1) and a rock (e). For the trans-$XPt(PEt_3)_2MH_3$ species the symmetry at silicon is lower and the degenerate modes may be split; the observed bands may then be assigned as shown below:

	antisymm. bends δ_5(MH)	symm. bend δ_2(MH)	rock δ_6(MH)
$ClPt(PEt_3)_2GeH_3$	905, 885 cm^{-1}	830 cm^{-1}	570 cm^{-1}
$ClPt(PEt_3)_2SiH_3$	970, 945 cm^{-1}	915 cm^{-1}	n.o.

The compounds with X = Br, I have infrared bands at similar frequencies which may be assigned to the same modes. The

silylcobaltcarbonyl and silylcobaltmanganese compounds, discussed in the introduction, have spectra in the ν(SiH) and δ(SiH) regions similar to the platinum compounds and the bands have been assigned in the same manner[5, 10].

The MX and PtX stretching frequencies come in characteristic regions, though the former are lower in the spectra of the solid compounds than in the vapour phase spectra of the parent halides. The relatively low values of ν(PtX) are consistent with the high trans influence of silicon and of germanium[29]. On the basis of a list formed by Chatt[30], it appears that $-SiH_2Cl$ and $-GeH_2Cl$ may have about the lowest trans influence of any silyl or germyl groups. The PtCl stretching frequency may not be a true indication of the trans influence however, for it may be coupled with a Pt-M stretching vibration.

Assignment of such bands in the far infrared is difficult because of the possibility of coupling between different skeletal modes of the same symmetry. Thus some of the above and all the following assignments are tentative, and the frequencies of the assigned bands may not represent the true values for uncoupled vibrations.

Two bands have been assigned to ν(PPtP). The band above 400 cm^{-1} may be the antisymmetric stretch: it is in a characteristic region for trans-triethylphosphine platinum

compounds[69,70]. The band below 400 cm^{-1} may be the symmetric stretch ν_s(PPtP), since it is very much more intense in the Raman spectrum. The symmetric stretch is also active in the infrared, despite the trans phosphines because the overall symmetry of the skeleton is less than D_{2h}. The frequency of this mode 380 cm^{-1}, is much lower than in trans-$ClPt(PEt_3)_2Cl$ where a band at 432 cm^{-1} was assigned to the metal phosphorous, symmetric stretch[71].

A band varying in position from 328 to 344 cm^{-1} is assigned to ν(PtSi). It is in close agreement with the value of 352 cm^{-1} for ν(PtSi) in trans-$ClPt(PEt_3)_2SiMe_3$[39]. A tentative assignment of ν(GePt) is made. When chlorine is bonded to platinum, the frequencies ν(GePt) and ν(PtCl) appear to be anomalous, possibly due to coupling.

The information available from infrared spectroscopy is fairly extensive, but in general n.m.r. spectroscopy was preferred for identification of compounds. N.M.R. has several advantages. The sample can be prepared for the spectrometer under vacuum thus minimising the possibility of decomposition, and the spectra can easily be run at low temperatures. The stereochemistry of a compound can be determined easily, whereas any determination by infrared is tentative and requires further confirmation. Mixtures of similar compounds are difficult to identify by infrared, but their n.m.r. spectra are usually well separated.

CHAPTER II

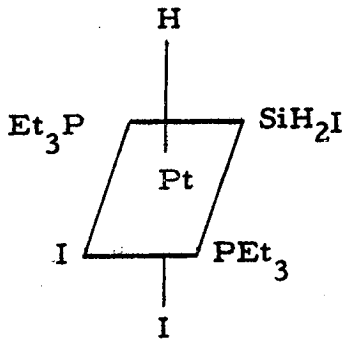
THE FORMATION OF SOME SIX-COORDINATED PLATINUM SPECIES AND SOME RELATED REACTIONS.

2.1 The reaction of trans-$IPt(PEt_3)_2I$ with MH_3X.

The formation of a silicon or germanium-platinum bond by the reaction of a silicon or germanium hydride with a four-coordinated platinum(II) compound has been postulated to occur through a six-coordinated intermediate, formed by addition of the M-H bond to platinum. Possible reaction schemes have been discussed in the introduction and in the previous chapter. The isolation of a silyl compound of six-coordinated platinum, which is produced in a similar reaction, is described below.

Silyl iodide reacts with trans-$IPt(PEt_3)_2I$, to form an equimolar adduct, soluble in benzene at room temperature:[87]

SiH_3I + trans-$IPt(PEt_3)_2I$ ⟶



The product has been formulated as the six-coordinated platinum(IV) compound shown above, on the basis of the n.m.r. spectrum. The HPt resonance at -15° shows coupling

to Pt^{195} and to two equivalent phosphorous atoms cis to platinum-hydrogen. The six-coordinated compound is assumed to be the product of cis addition of IH_2Si-H because no coupling between HPt and $-SiH_2I$ is observed. In related compounds (described in Chapter V) J(trans H PtMH_2X) is about 10 Hz. A feature of the n.m.r. spectra which appears to be characteristic of six-coordinated platinum compounds is the low value of J(HPt^{195}) and J(HMPt^{195}) compared with the coupling constants for similar compounds of four-coordinated platinum. The n.m.r. parameters are shown, together with those of related compounds, in Table 2.1.

The six-coordinated product decomposes slowly at room temperature as described in section 2.3, but it can be isolated as a pale yellow, crystalline solid by careful evaporation of the solvent at -22°. In contrast to the slow decomposition in solution there is no evidence for similar decomposition of the solid, which has been further characterised by analysis and by Raman and infrared spectra. The infrared spectrum is very similar to that of the four-coordinated compound trans-$IPt(PEt_3)_2SiH_2I$ except that there is a new band in the δ(SiH) region and a band with a shoulder in the ν(SiH) region. In the Raman spectrum there are two new high frequency bands, and two new bands on the side of the Rayleigh line which may possibly be assigned to the IPtI

Table 2.1

Parameters from the M$\underline{H}$ and Pt$\underline{H}$ proton resonance spectra (M = Si or Ge) of $I_2Pt(PEt_3)_2H.Z$, measured for benzene/T.M.S. solutions at -15° relative to T.M.S.

Z	τ(M$\underline{H}$) ppm	J(H$\underline{M}$P$\underline{t}$) Hz	J(H$\underline{M}$Pt$\underline{P}$) Hz	τ(H$\underline{P}$t) ppm	J(H$\underline{P}$t) Hz	J(HPt$\underline{P}$) Hz
SiH_2Cl	5.19	62.8[a]	7.8	23.4	1185[b]	5.5
SiH_2I	5.93	59.2[c]	7.6	24.6	1160	6
GeH_2I	6.52	119[d]	7.1	23.8	1111.2	5

a) in trans-$IPt(PEt_3)_2SiH_2Cl$ J(H$\underline{M}$P$\underline{t}$) = 123.8

b) in trans-$IPt(PEt_3)_2H$[116] J(H$\underline{P}$t) = 1369

c) in trans-$IPt(PEt_3)_2SiH_2I$ J(H$\underline{M}$P$\underline{t}$) = 127.1

d) in trans-$IPt(PEt_3)_2GeH_2I$ J(H$\underline{M}$P$\underline{t}$) = 221.2

stretching vibrations. The new infrared and Raman frequencies are shown with tentative assignments in Table 2.2; some frequencies of similar modes in related compounds have been included for comparison. The frequency ν(Si-H) for a wide range of four-coordinated platinum silyl compounds is about 2110 cm^{-1}, and the higher value is a useful distinguishing feature of six-coordinated complexes.

The reactions of SiH_3Cl and GeH_3I with trans-$IPt(PEt_3)_2I$ give six-coordinated compounds similar to $I_2Pt(PEt_3)_2H.SiH_2I$. The products have been identified by n.m.r. spectroscopy and the parameters obtained are listed in Table 2.1.

2.2 The reactions of HI with trans-$IPt(PEt_3)_2MH_2X$.

The reactions of hydrogen halides with silyl and germyl-platinum compounds have also been accounted for in terms of six-coordinated intermediates, though none have been isolated[30, 46, 60]. Hydrogen iodide reacts immediately at room temperature with trans-$IPt(PEt_3)_2MH_2X$ forming an equimolar adduct. The adducts are the same as the six-coordinated platinum compounds discussed in section 2.1.

HI + trans-$IPt(PEt_3)_2MH_2X$ ⟶

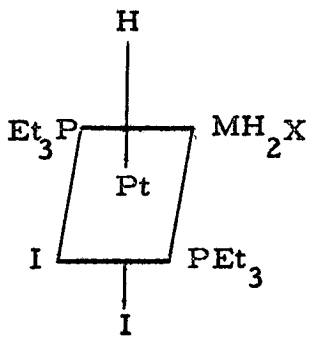


Table 2.2

The new frequencies in the Raman and infrared spectra of $I_2Pt(PEt_3)_2H.SiH_2I$ in comparison with some frequencies of related compounds.

Compound	Tentative assignments					
	ν(PtH) cm^{-1}		ν(SiH) cm^{-1}		δ(PtH) cm^{-1}	ν(PtI) cm^{-1}
	R.	I.R.	R.	I.R.	I.R.	R.
$I_2Pt(PEt_3)_2H.SiH_2I$	2235 m	2200 sh	2192 s,	2160 s	860 m	175 w, 130 w
$IPt(PEt_3)_2SiH_2I$	-		2144 s,	2120 s		148 s
$IPt(PEt_3)_2H$	2193	2156[52]			n.a.	151

R = Raman; I.R. = infrared; s = strong; w = weak; m = medium intensity; sh = shoulder; n.a. = not assigned, there are only two weak bands in this region at 800 and 820 cm^{-1}.

The initial n.m.r. spectra at room temperature of solutions of trans-$IPt(PEt_3)_2MH_2X$ containing less than an equimolar proportion of HI showed some unexpected effects. As the molar proportion Q(HI : $IPt(PEt_3)_2MH_2X$) increased from O, the main MH resonance and the Pt^{195} satellites showed differential broadening. A representation of the spectra obtained when M = Si, X = I, is shown in Figure 2.1. The low-field Pt^{195} satellite remained a relatively sharp triplet for all values of Q and only shifted in position by a small amount. As Q increased from O to O.5, the main resonance shifted to low field and broadened, but retained a triplet pattern; as Q increased further from O.5 to 1, it shifted further to low field but sharpened. The high-field Pt^{195} satellite broadened and collapsed completely as Q increased from O, until as Q approached 1 it appeared as a sharp triplet and the overall spectrum was that corresponding to the six-coordinated adduct $I_2Pt(PEt_3)_2H.SiH_2I$. When the solution in which Q = O.5 was cooled to -10°, the broad main resonance separated into two sharp triplets corresponding to trans-$IPt(PEt_3)_2SiH_2I$ and $I_2Pt(PEt_3)_2H.SiH_2I$. This behaviour is consistent with an exchange of HI that is fast at room temperature on the n.m.r. time-scale, but slow at -10°:

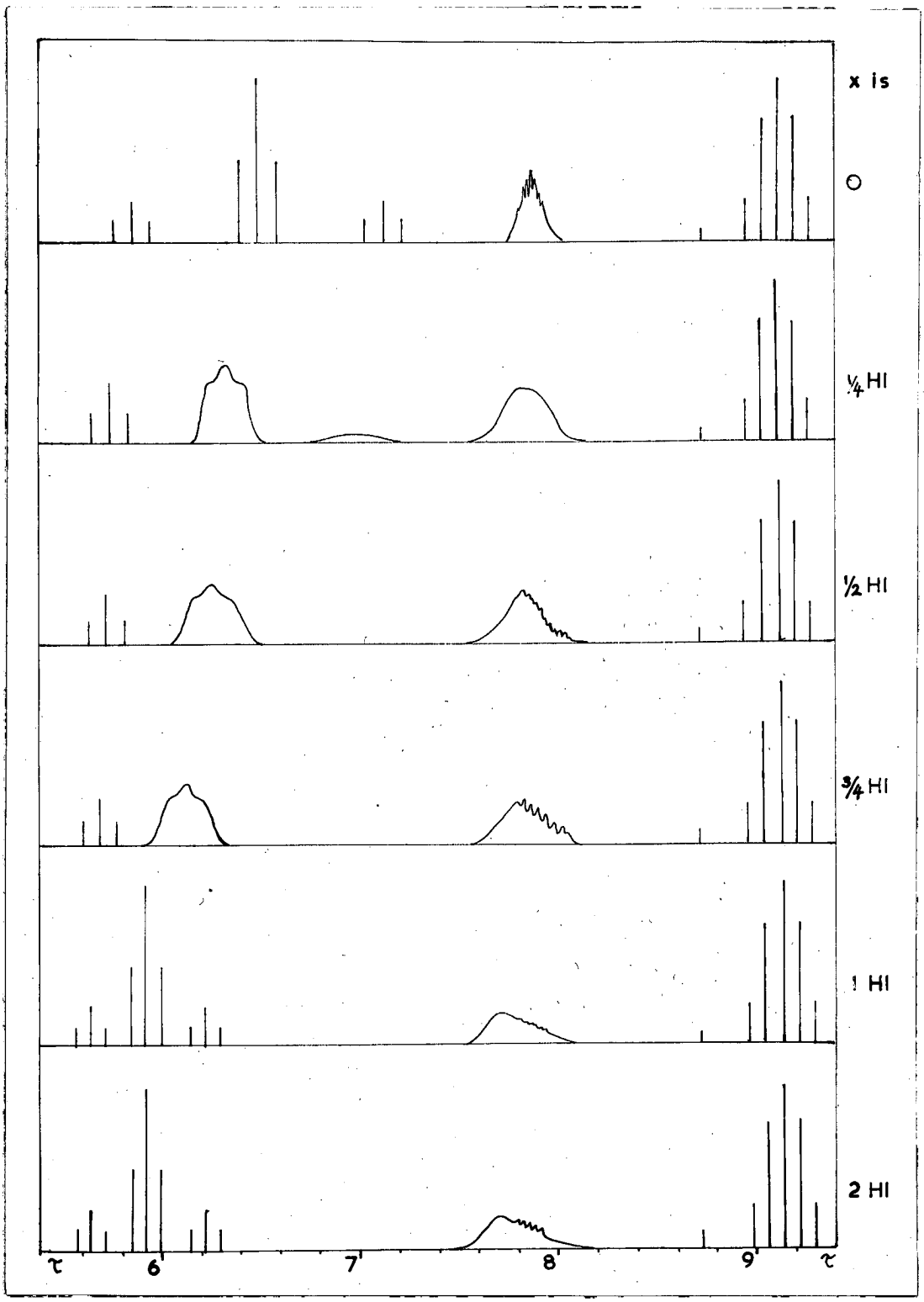


Figure 2.1

Some proton n.m.r. spectra of reactions between 1 molar portion of $IPt(PEt_3)_2SiH_2I$ and x molar portions of HI. The intensity of the phosphine resonances is not drawn to scale.

$$IPt(PEt_3)_2SiH_2I + \begin{matrix} H \\ | \\ IPt(PEt_3)_2SiH_2I \\ | \\ I \end{matrix} \rightleftharpoons \begin{matrix} H \\ | \\ IPt(PEt_3)_2SiH_2I \\ | \\ I \end{matrix} + IPt(PEt_3)_2SiH_2I$$

In this reaction the SiPt and PtP bonds remain unbroken, and hence in the fast exchange situation the n. m. r. spectrum will have peaks in the average positions of those due to the four-coordinated and six-coordinated compounds, the $\underline{H}MP\underline{t}^{195}$ and the $\underline{H}MPt\underline{P}$ couplings being retained. Because of the values of $\tau(\underline{H}Si)$ and $J(\underline{H}Si\underline{P}t^{195})$ it happens that at 100 MHz the low field satellites for the two compounds almost coincide, and fast exchange results in a sharp peak. The positions of the high field satellites for the two compounds differ considerably and hence exchange leads to broadening which is, under some conditions, sufficiently large to prevent detection of the resonance. The difference in chemical shifts of the two main peaks and the subsequent broadening lies between these two extremes. A similar pattern of broadening is observed for mixtures of trans-$IPt(PEt_3)_2SiH_2Cl$ and HI.

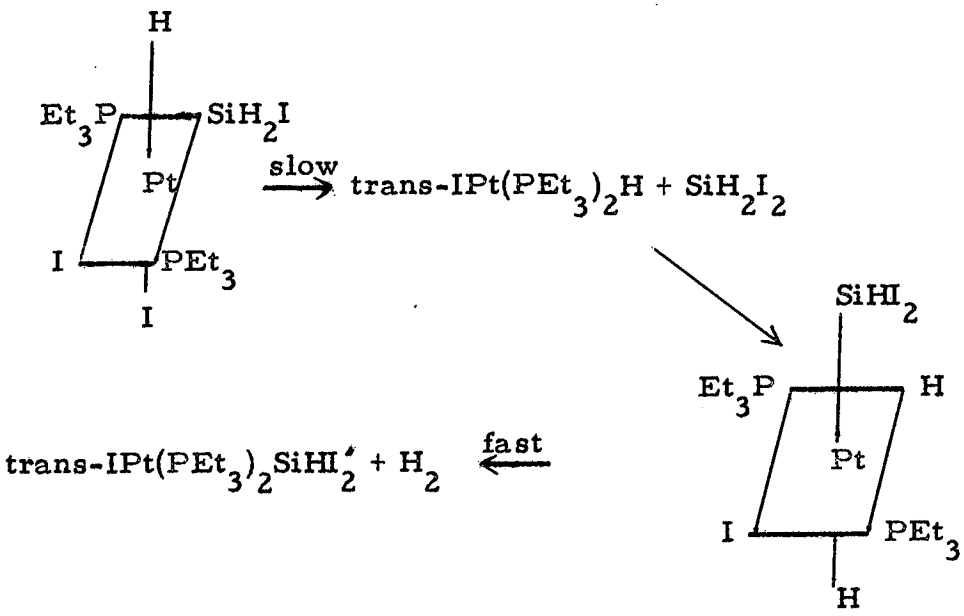
In the spectrum of a mixture of HI and trans-$IPt(PEt_3)_2GeH_2I$ the chemical shift $\tau(\underline{H}Ge)$ is the same for both the four-coordinated compound and the HI adduct. The result is that the main triplet remains sharp, while both the

platinum satellites broaden and move out as the proportion of HI decreases from 1.

The parameters associated with the HPt resonances listed in Table 2.1 were obtained at -15°. Use of low temperature n.m.r. is necessary because the HPt resonance is broad at room temperature, possibly due to an exchange similar to that discussed above. At -15° the six-coordinated species are also stable towards the decomposition which occurs at room temperature.

2.3 Decomposition of the six-coordinated platinum compounds.

The intermediates thought to be produced by addition of HCl to platinum compounds are postulated (as mentioned in the introduction) to decompose by elimination of a silicon or germanium hydride or halide. The six-coordinated complex $I_2Pt(PEt_3)_2H.SiH_2I$ decomposes slowly in benzene solution with evolution of hydrogen and formation of trans-$IPt(PEt_3)_2SiHI_2$. The reaction may occur by slow elimination of SiH_2I_2, followed by readdition of Si-H and rapid elimination of H_2, as in the preparative reaction described in Chapter I.



The identification of SiH_2I_2 in a sample of the six-coordinated compound which had not completely decomposed affords some evidence for this mechanism. The SiH_2I_2 disappeared after about one week when trans-$IPt(PEt_3)_2SiHI_2$ was the only silyl species whose n.m.r. spectrum was detected. After decomposition has begun the n.m.r. spectrum of $I_2Pt(PEt_3)_2H.SiH_2I$ shows broadening of the high field Pt^{195} satellite and the main triplet, just as in the exchange discussed in the previous section. The broadening may therefore be accounted for by some loss of HI from the adduct (perhaps combining with trans-$IPt(PEt_3)_2H$), leaving a mixture of $IPt(PEt_3)_2SiH_2I$ and $I_2Pt(PEt_3)_2H.SiH_2I$.

The six-coordinated compounds $I_2Pt(PEt_3)_2H.SiH_2Cl$ and $I_2Pt(PEt_3)_2H.GeH_2I$ decompose in a similar manner. The former compound gives mixed halogen species which appear from consideration of the n.m.r. parameters,

to be trans-$IPt(PEt_3)_2SiHX_2$. Decomposition of $I_2Pt(PEt_3)_2H.GeH_2I$ is accompanied by production of a brown tar, perhaps related to the similar thermal decomposition of trans-$IPt(PEt_3)_2GeH_2I$ described in Chapter I.

2.4 The reaction of HCl with trans-$ClPt(PEt_3)_2SiH_2Cl$.

The reaction of HI with trans-$IPt(PEt_3)_2SiH_2I$ results, after about one week, in the formation of trans-$IPt(PEt_3)_2SiHI_2$ and hydrogen. Hydrogen chloride reacts completely in five minutes at room temperature in benzene with an equimolar amount of trans-$ClPt(PEt_3)_2SiH_2Cl$:

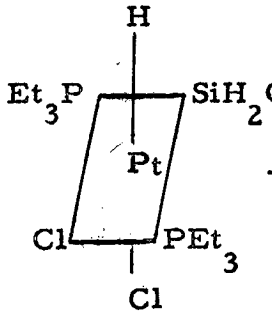
$$HCl + \text{trans-}ClPt(PEt_3)_2SiH_2Cl \longrightarrow \text{trans-}ClPt(PEt_3)_2SiHCl_2 + H_2$$

The reaction was judged to be quantitative because the amount of hydrogen evolved, measured using a Toepler pump, was found to be in equimolar proportion to the amount of HCl added. The product was the same as the compound produced by reaction of SiH_2Cl_2 with trans-$ClPt(PEt_3)_2H$. On the basis of the similarity in reactants and products with the hydrogen iodide reaction, it seems reasonable to assume that the HCl reaction occurs by formation of a six-coordinated intermediate, $Cl_2Pt(PEt_3)_2H.SiH_2Cl$, which then decomposes in the same manner as described for the HI adduct in section 2.3. The compound trans-$ClPt(PEt_3)_2SiHCl_2$ also reacts with HCl and further substitution of H by Cl at silicon occurs. The reaction is complete after two days and does not proceed

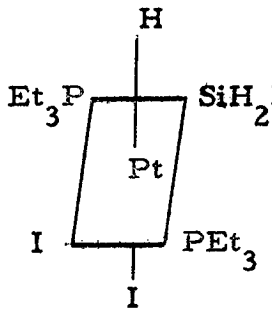
any further under these conditions, even with a large excess of HCl:

$$trans\text{-}ClPt(PEt_3)_2SiHCl_2 + HCl \longrightarrow trans\text{-}ClPt(PEt_3)_2SiCl_3 + H_2$$

The products were identified by infrared spectroscopy and by the amount of H_2 evolved. Again it seems likely that the reaction proceeds by a similar mechanism to that of HI and $trans\text{-}IPt(PEt_3)_2SiH_2I$. The rates of reaction of HCl and HI are very different, however, and no intermediates have been detected in the HCl reactions even at -60°; if intermediates are formed they must decompose fast. This behaviour may be understood if the rate-determining step in the reactions is decomposition of the six-coordinated intermediates:



$$\xrightarrow{\text{fast}} SiH_2Cl_2 + trans\text{-}ClPt(PEt_3)_2H$$



$$\xrightarrow{\text{slow}} SiH_2XI + trans\text{-}IPt(PEt_3)_2H$$

(X = Cl, I)

The fast formation of the silicon-chlorine bond in SiH_2Cl_2 in comparison with the slow formation of the silicon-iodine

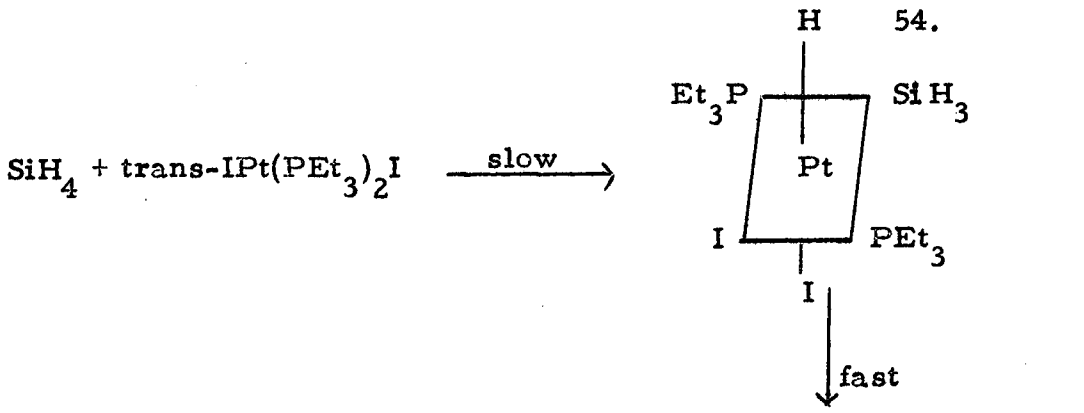
bond in SiH_2XI may be related to the greater strength of the SiCl bond in comparison with the SiI bond. Some bond energies supporting this order have been quoted in Chapter I section 1.2, where it was also suggested that the platinum-iodine bond may be stronger than the platinum-chlorine bond. These differences in the silicon-halogen and platinum-halogen bond strengths would both enhance the stability of the six-coordinated HI adduct relative to the stability of the HCl adduct, with respect to elimination of a silicon-halogen species. Although the mechanism involving oxidative addition of HCl to Pt described above seems most probable, the possibility of a different mechanism, perhaps involving direct cleavage of the PtSi bond by HCl cannot be ruled out. Hydrogen chloride reacts with $SiH_3Mn(CO)_5$ at 75° successively replacing H by Cl at silicon. The formation of an intermediate similar to that postulated for the silyl-platinum compounds is impossible and the reaction probably involves direct cleavage of the SiH bonds. However, the fact that this reaction only occurs on heating to 75°, whereas the halogenation of a silyl-platinum compound is fast at room temperature, suggests that the latter may not involve similar direct cleavage of SiH.

2.5 Some reactions of silyl and germyl compounds with $(PEt_3)_2PtX_2$.

Silyl iodide and germyl iodide react immediately, even at 0°, with trans-$IPt(PEt_3)_2I$ to form the six-coordinated platinum(IV) adducts described in section 2.1. The reactions of monosilane and monogermane with platinum(II) hydrides are slower than the reactions of the monohalogen-substituted derivatives. These reactions have been discussed in Chapter I section 1.3 in terms of electrophilic attack at platinum. In accordance with this difference in rates of reaction SiH_4 and GeH_4 react only very slowly at 0° with trans-$IPt(PEt_3)_2I$, but the reaction is faster at room temperature being complete after 15 minutes:

$$MH_4 + \text{trans-}IPt(PEt_3)_2I \longrightarrow \text{trans-}IPt(PEt_3)_2MH_2I + H_2$$

The reaction, which involves immediate evolution of hydrogen, contrasts with the reaction of MH_3I. Despite the lack of any direct evidence in the case of MH_4, the differences can again be explained in terms of six-coordinated intermediates. Silyl and germyl iodide react quickly forming a Pt(IV) intermediate which decomposes slowly, whereas MH_4 may react comparatively slowly to form a Pt(IV) intermediate which decomposes fast. A possible reason for the slow reaction has been mentioned; the fast decomposition in comparison with $I_2Pt(PEt_3)_2H.MH_2X$ may be for steric reasons:



Formation of SiH_3I from $-SiH_3$ is less hindered sterically than formation of SiH_2I_2 from $-SiH_2I$.

Silyl chloride reacts slowly with trans-$ClPt(PEt_3)_2Cl$. The reaction, which has been studied by n.m.r. spectroscopy, is complete after ten days with the formation of H_2 and trans-$ClPt(PEt_3)_2SiHCl_2$. Dichlorosilane and trans-$ClPt(PEt_3)_2SiH_2Cl$ have been detected at intermediate stages in the reaction, which therefore follows a close parallel to that of SiH_3I with trans-$IPt(PEt_3)_2I$. Thus the reaction may involve addition of SiH to Pt, forming a six-coordinated intermediate which is the same as that proposed for the reaction of HCl with trans-$ClPt(PEt_3)_2SiH_2Cl$. As before there is no direct evidence for such an intermediate; it must be formed slowly and decompose fast. The implied slow formation of the six-coordinated intermediate contrasts with the rapid reaction between SiH_3Cl and trans-$IPt(PEt_3)_2I$, and indicates that electrophilic attack at platinum may be important.

Germyl chloride reacts in a different manner with trans-$ClPt(PEt_3)_2Cl$. The reaction is consistent with initial slow formation of trans-$ClPt(PEt_3)_2GeH_2Cl$ and trans-$ClPt(PEt_3)_2GeHCl_2$, in an analogous manner to the reaction with SiH_3Cl, followed by further reaction with the excess GeH_3Cl as described in Chapter V.

Monosilane also reacts with trans-$ClPt(PEt_3)_2Cl$ in a manner analogous to SiH_3Cl but more slowly: only a little trans-$ClPt(PEt_3)_2SiH_2Cl$ is formed after one week.

With cis-$(PEt_3)_2PtCl_2$ in benzene, SiH_3Cl reacts very slowly, possibly due to the low solubility of the cis reactant, forming a mixture of trans products $ClPt(PEt_3)_2SiH_2Cl$ and $ClPt(PEt_3)_2SiHCl_2$. The reaction is incomplete even after one month when some brown tar is formed.

2.6 The reaction of SiH_3Cl with trans-$ClPd(PEt_3)_2Cl$.

Silyl chloride reacts slowly with trans-$ClPd(PEt_3)_2Cl$ in benzene at room temperature. The n.m.r. spectrum of the reaction mixture indicates the presence of unreacted SiH_3Cl, SiH_2Cl_2 and other silyl species associated with two 1:2:1 triplets. By analogy with the reaction of SiH_3Cl and trans-$ClPt(PEt_3)_2Cl$ the triplets are assigned as shown below:

compound	τ p.p.m.	$J(\underline{H}SiPd\underline{P})$ Hz
trans-$ClPd(PEt_3)_2SiH_2Cl$	5.15	14.3
trans-$ClPd(PEt_3)_2SiHCl_2$	4.19	18.2

The similarity of this reaction with the $ClPt(PEt_3)_2Cl$ and $IPt(PEt_3)_2I$ reactions does seem to imply that the reaction takes place by slow oxidative addition of SiH to palladium forming a six-coordinated intermediate, from which there is rapid elimination of HCl or SiH_2Cl_2. Although palladium does not form stable six-coordinated compounds with oxidation state(IV) as readily as platinum an example of a reaction postulated to occur by a similar addition-elimination reaction has been reported[72, 73]:

$$(bipy)PdMe_2 + C_3F_7I \longrightarrow (bipy)PdMe.C_3F_7 + (MeI)$$

However, the differences in the reactions of HCl and H_2 with $(PEt_3)_2Pt(SiPh_3)_2$ and with $(PEt_3)_2Pd(SiPh_3)_2$ have been interpretated in terms of addition-elimination reactions for the former, and possible direct cleavage reactions for the latter[59]:

e.g. $$(PEt_3)_2Pt(SiPh_3)_2 \xrightarrow{HCl} ClPt(PEt_3)_2H + Ph_3SiH + Ph_3SiCl$$

$$(PEt_3)_2Pd(GePh_3)_2 \xrightarrow{HCl} ClPt(PEt_3)_2Cl + 2Ph_3GeH$$

The differences in the reactions are not great, however, and may perhaps best be explained in terms of similar addition-elimination mechanisms. Nevertheless, the possibility that the reaction of SiH_3Cl with trans-$ClPd(PEt_3)_2Cl$ (and hence also the reaction of SiH_3Cl with trans-$ClPt(PEt_3)_2Cl$) takes place by a different reaction mechanism from

oxidative addition cannot be discounted.

An attempt was made to investigate the reaction of trans-$IPd(PEt_3)_2I$ with SiH_3X where, by analogy with the platinum compounds, formation of a six-coordinated intermediate should be more favourable, but any reaction was slow and was accompanied by decomposition together with the formation of a black solid, possibly palladium metal.

CHAPTER III.

SOME REACTIONS OF TRANS-$ClPt(PEt_3)_2SiH_2Cl$.

The reactions of trans-$ClPt(PEt_3)_2SiH_2Cl$(I) which have been studied can be divided very roughly into two categories: reactions involving the silyl group and reactions involving the other ligands joined to platinum. They are dealt with in that order.

Hydrogen chloride reacts with (I) in benzene at room temperature in a manner which has been discussed in Chapter II. Hydrogen is evolved and silicon is successively chlorinated until the final product is trans-$ClPt(PEt_3)_2SiCl_3$. With an excess of HCl at 100° the reaction proceeds no further; however, if solid (I) is treated with liquid HCl the platinum-silicon bond is cleaved permanently and $SiHCl_3$ is evolved, leaving a solid residue consisting mainly of $Cl_2Pt(PEt_3)_2H_2$ with some trans-$ClPt(PEt_3)_2SiCl_3$.

Methanol reacts with an equimolar amount of (I) in benzene and hydrogen is evolved. Other volatile reaction products which have been identified are silane, dichlorosilane, trimethoxysilane and a mixture of methoxychlorosilanes. The reported data concerning methoxychlorosilanes is limited and they have not been investigated very fully, possibly because they are unstable with respect to disproportionation; their identification in this system is therefore tentative. The infrared

spectra indicated the presence of $MeOSiH_2Cl$ and $(MeO)_2SiHCl$[74] together with SiH_2Cl_2 and SiH_4. The n.m.r. spectra indicated that SiH_2Cl_2 and SiH_4 were present, with three methoxysilyl compounds whose n.m.r. spectra are tentatively assigned below in Table 3.1. The values of the chemical shifts are noted together with the approximate ratio of intensity of the proton resonance $C\underline{H}_3O$: $Si\underline{H}$. This ratio may be used as a rough guide to the nature of the compound.

Table 3.1

Tentative assignment.	$\tau(\underline{H}_3CO)$ p.p.m.	$\tau(\underline{H}Si)$ p.p.m.	Approximate intensities $C\underline{H}_3O/\underline{H}Si$.
$(MeO)SiH_2Cl$	6.70	5.37	2:1
$(MeO)SiHCl_2$	6.75	5.04	4:1
$(MeO)_3SiH$	6.63	5.54	9:1

The correlation of a peak in the silyl region with a peak in the methoxy region was aided by the change in relative intensities of the peaks with the change in relative amounts of each methoxysilane in a series of experiments. For each compound the ratio $C\underline{H}_3O$: $\underline{H}Si$ remained constant. The involatile residue from the reaction was investigated by n.m.r. and infrared spectroscopy. The n.m.r. spectrum indicated the presence of a silyl platinum compound having the parameters listed in Table 3.2; this could be trans-$ClPt(PEt_3)_2SiHCl(OMe)$. The ratio of intensities $C\underline{H}_3O$: $\underline{H}Si$ = 1.6 : 1 is in agreement with this proposal. The infrared spectrum of the residue suggests

Table 3.2

Parameters from the HSi proton resonance spectra of some compounds produced by reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$. The parameters are measured in benzene solution at room temperature.

Compound	τ(HSi) ppm	τ(HC) ppm	J(HSiPt) Hz	J(HSiPtP) Hz
trans-$ClPt(PEt_3)_2SiHCl(OCH_3)$	4.12	6.46	128.3	8.5
trans-$ClPt(PEt_3)_2SiH_2(OCH_3)$	4.80	6.51	102	n.o.
trans-$ClPt(PEt_3)_2SiH_2N(CH_3)_2$	5.54	7.30	78.3	8.4
[trans-$ClPt(PEt_3)_2SiH_2S(S)CN(CH_3)_2$]	4.99	7.23	108	n.o.

that the material is a mixture of trans-$ClPt(PEt_3)_2H$ and another compound, which could well be trans-$ClPt(PEt_3)_2SiHCl(OMe)$. The nature of these products suggests that methanol may attack the silicon-chlorine bond liberating HCl.

$$\text{trans-}ClPt(PEt_3)_2SiH_2Cl + MeOH \longrightarrow \text{trans-}ClPt(PEt_3)_2SiH_2(OMe) + HCl.$$

The HCl may then attack the methoxysilylplatinum compound as it would a halogenosilylplatinum derivative forming the platinum hydride and $(MeO)SiH_2Cl$. The methoxysilylchloride may then either react with the platinum hydride in the usual way forming trans-$ClPt(PEt_3)_2SiHCl(OMe)$ and hydrogen, or disproportionate to the mixture of silanes and methoxysilanes detected in the reaction.

The reaction with methanol in the presence of trimethylamine is less complicated. No hydrogen is evolved and the products appear to be consistent with replacement of Cl- by MeO- at silicon forming HCl which is removed as the trimethylammonium salt.

$$\text{trans-}ClPt(PEt_3)_2SiH_2Cl + MeOH + Me_3N \longrightarrow \text{trans-}ClPt(PEt_3)_2SiH_2(OMe) + Me_3NH^+Cl^-$$

The n.m.r. and infrared spectra of the product are in agreement with this assignment. The lines in the n.m.r. spectrum, which is a 1 : 4 : 1 triplet, are broad and the HSiPtP coupling is not observed; the other parameters are listed in Table 3.2. The

same broadening effect is observed when a benzene solution of trans-$ClPt(PEt_3)_2SiH_2Cl$ is treated with a small amount of Me_3N; a possible reason is suggested later.

Water reacts rapidly with (I), the ultimate products being hydrogen, silica and $Cl_2Pt(PEt_3)_2H_2$. These reactions with water, MeOH and liquid HCl are the only reactions involving significant permanent cleavage of the platinum-silicon bond. In each case the cleavage may be caused by HCl, which may act by formation of a six-coordinated intermediate as described in Chapter II.

Though (I) is very sensitive to moisture, it only reacts very slowly with dry oxygen forming a little platinum hydride. This reaction contrasts greatly with the silyl-transition metal carbonyl complexes such as $SiH_3Co(CO)_4$ and $SiH_3Mn(CO)_5$[5, 10, 12] which sometimes react violently with oxygen. All the SiH compounds are thermodynamically unstable with respect to oxidation so kinetic factors must be involved.

When a two-fold excess of dimethylamine is slowly added to trans-$ClPt(PEt_3)_2SiH_2Cl$ in toluene at -22° a white precipitate of $Me_2NH_2^+Cl^-$ is formed:

$$\text{trans-}ClPt(PEt_3)_2SiH_2Cl + 2Me_2NH \longrightarrow \text{trans-}ClPt(PEt_3)_2SiH_2NMe_2 + Me_2NH_2^+Cl^-$$

The precipitate can be filtered off and on evaporation of the

solvent at -22° the product remains as a pale brown sticky paste, which is thermally quite stable, though in solution at room temperature it gradually turns dark brown and decomposes in about one hour. It has been characterised by analysis and by infrared and n.m.r. spectroscopy. The n.m.r. parameters are listed in Table 3.2. An attempt was made to prepare the same platinum compound from SiH_3NMe_2 and trans-$ClPt(PEt_3)_2H$ but this reaction resulted only in a brown tar. Carbon disulphide and related compounds react with the parent silyl compound SiH_3NMe_2, inserting into the silicon-nitrogen bond. (e.g. CS_2 forms $SiH_3S(S)CNMe_2$[75]). The reactions of the platinum compounds trans-$ClPt(PEt_3)_2SiH_2NMe_2$ with CO_2, COS and CS_2 were studied in order to investigate the possibility of a similar reaction. No decisive evidence was obtained for any reaction because of complications due to rapid decomposition, but there was some evidence from the n.m.r. spectra that CS_2 did insert. The n.m.r. parameters of the possible complex trans-$ClPt(PEt_3)_2SiH_2.S(S)C.NMe_2$ are quoted in Table 3.2; no HSiPtP coupling was observed in the spectrum, though the lines were sharp. Treatment of trans-$ClPt(PEt_3)_2SiH_2NMe_2$ with MeI at -22° in toluene resulted in a slow precipitation of a white solid, presumably due to quarternisation at nitrogen. No spectroscopic evidence was obtained to establish its nature because it decomposed on warming to room temperature.

The addition of triethylphosphine to a benzene solution of (I) causes collapse of the coupling J(HSiPtP) together with apparent simplification of the resonances due to ethyl protons. These results suggest that there is exchange between free and bound Et_3P which is fast on the n.m.r. time-scale; the platinum-silicon bonds are preserved because there is no collapse of the coupling J(HSiPt^{195}). With small amounts of Et_3P the resonance associated with CH_3- protons is approximately a triplet and that associated with CH_2- protons approximates to a quartet, suggesting that rapid exchange has caused collapse of the CH_3CH_2P and CH_3CH_2P couplings. The spectrum is shown in Figure 3.1. A similar collapse in coupling has been observed in some trimethylphosphine-palladium complexes and is theoretically consistent with chemical exchange of Me_3P[76].

With phosphine and (I) in benzene, a white solid is slowly precipitated from the solution, accompanied by collapse of the ethyl resonance into peaks with approximate quartet and triplet patterns. Thus phosphine may slowly replace Et_3P from (I) forming an insoluble platinum-phosphine complex, though the white solid was too unstable for any identification.

In several n.m.r. spectra of (I) and related compounds the coupling J(HSiPtP) is completely or partly collapsed whereas the coupling J(HSiPt^{195}) is retained. This collapse may be due, in each case, to a little Et_3P which may be produced by reaction or by decomposition. Thus with Me_3N and C_2H_4

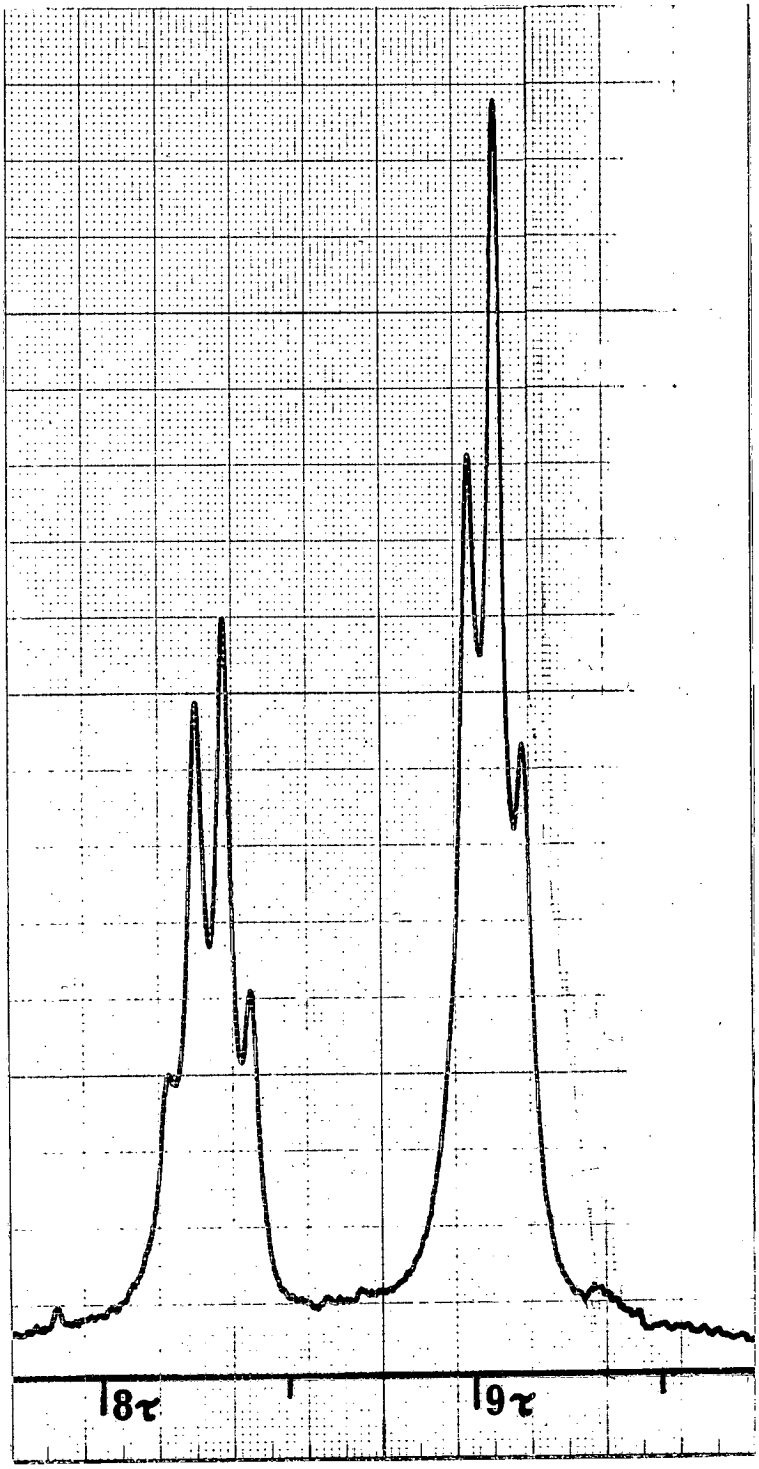


Figure 3.1

Triethylphosphine resonance pattern in the n.m.r. spectrum of a mixture of trans-$ClPt(PEt_3)_2SiH_2Cl$ and Et_3P.

there is no apparent reaction at room temperature, except for partial collapse of J(HSiPtP). After an equimolar amount of Me_3N has been added to a benzene solution of (I) and allowed to mix at room temperature for one hour, 95% of the Me_3N is recovered unchanged. This lack of reaction contrasts with the reaction of $SiH_3Co(CO)_4$ and related compounds, which form adducts under these conditions[7]. For some compounds, prone to decomposition, the coupling J(HSiPtP) was completely collapsed e.g. trans-$ClPt(PEt_3)_2SiH_3$ and the putative trans-$ClPt(PEt_3)_2SiH_2S(S)C.NMe_2$. When the former compound was prepared at -22° in toluene there was no broadening or collapse of the HSi resonance and J(HSiPtP) could be measured, perhaps because decomposition and release of Et_3P is arrested at low temperatures. The exchange with Et_3P may involve a five-coordinated platinum intermediate, but lowering of the temperature to -30° failed to produce any evidence as the exchange was still fast. Formation of a similar intermediate and consequent phosphine exchange may be less likely with a six-coordinated platinum compound. In order to test this supposition the compound $I_2Pt(PEt_3)_2H.SiH_2I$ was treated with Et_3P, but the only result was removal of HI as $Et_3PH^+I^-$ and formation of the four-coordinated compound trans-$IPt(PEt_3)_2SiH_2I$. This reaction is similar to the method described in the introduction for the preparation of SiPt bonds, involving removal of HCl by

Et_3N[30] from a postulated , similar six-coordinated intermediate.

On prolonged standing in the presence of silyl halide a benzene solution of (I) separates into two phases; the proton resonances in the n.m.r. spectrum broaden and eventually disappear. Infrared spectra show that each phase contains benzene and a platinum silyl compound. On evaporation of benzene from the lower phase, which contains most of the platinum, a sticky, colourless and very viscous deposit remains. The nature of this product is not understood but may be polymeric.

In contrast to the reaction of methyl iodide with trans-$IPt(PEt_3)_2Me$ forming a six-coordinated product $I_2Pt(PEt_3)_2Me_2$,[34] reaction with (I) results only in halogen exchange:

$$MeI + \text{trans-}ClPt(PEt_3)_2SiH_2Cl \longrightarrow \text{trans-}IPt(PEt_3)_2SiH_2Cl + MeCl.$$

The reaction is slow at room temperature and may possibly occur either by an addition-elimination or substitution reaction.

CHAPTER IV.

SOME PLATINUM SUBSTITUTED DISILYL AND DIGERMYL COMPOUNDS.

4.1. Introduction

Disilane was characterised by Stock[77] in 1916 but it was not until quite recently that methods were developed for preparing pure halogen derivatives. MacDiarmid first used the reaction with AlI_3 and HI[78]:

$$Si_2H_6 + HI \xrightarrow{AlI_3} Si_2H_5I + H_2$$

He later prepared Si_2H_5Cl by treatment of disilane with boron trichloride[79]. This reaction, which was developed by Drake[80], is a very convenient method for the preparation of Si_2H_5Cl, $Si_2H_4Cl_2$ and $Si_2H_3Cl_3$. By changing the reaction conditions the relative amount of the required halogenated disilane can be increased and it can then be separated from the other products by fractional condensation in a vacuum line. The BCl_3 is quantitatively converted into B_2H_6 which is easily removed, being much more volatile than the disilane derivatives.

Digermane was first characterised in 1924[81]. It is thermally less stable than disilane; the GeH bond energy is lower than that for SiH and the GeGe bond is weaker than the SiSi bond. (In M_2H_6 E(GeGe) = 38.2 kcal/mole, E(SiSi) = 46.4 kcal/mole[16]). The mono-substituted derivatives of

of Ge_2H_6 are also much less stable than the analogous disilanyl compounds and they decompose rapidly in the liquid phase, though they are stable as gases. Ge_2H_5Cl is conveniently prepared by passing Ge_2H_6, diluted with n-pentane, over heated AgCl[82]. A preliminary study of the reactions of these compounds with platinum hydrides is described below.

4.2 The reactions of some disilyl and digermyl compounds with some platinum(II) complexes.

When Si_2H_6 or Si_2H_5Cl is treated with trans-$ClPt(PEt_3)_2H$, hydrogen is evolved and there is immediate separation into two phases. The two phase system resembles that which is produced in the reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with SiH_3Cl and the nature of the system is not understood. With Ge_2H_6, however, an equimolar amount of trans-$ClPt(PEt_3)_2H$ reacts to form a digermanyl platinum compound:

$$Ge_2H_6 + \text{trans-}ClPt(PEt_3)_2H \longrightarrow \text{trans-}ClPt(PEt_3)_2Ge_2H_5 + H_2.$$

The product has been identified by the amount of hydrogen evolved and by the n.m.r. spectrum, a representation of which is shown in Figure 4.1. The n.m.r. parameters are shown in Table 4.1. The product, in benzene solution at room temperature, rapidly turns brown and decomposes completely in about 15 minutes.

Though Si_2H_6 forms a two phase system with trans-$ClPt(PEt_3)_2H$, it reacts with an equimolar portion of trans-$IPt(PEt_3)_2H$ to form a disilanyl compound:

$$Si_2H_6 + \text{trans-}IPt(PEt_3)_2H \longrightarrow \text{trans-}IPt(PEt_3)_2Si_2H_5 + H_2.$$

Table 4.1

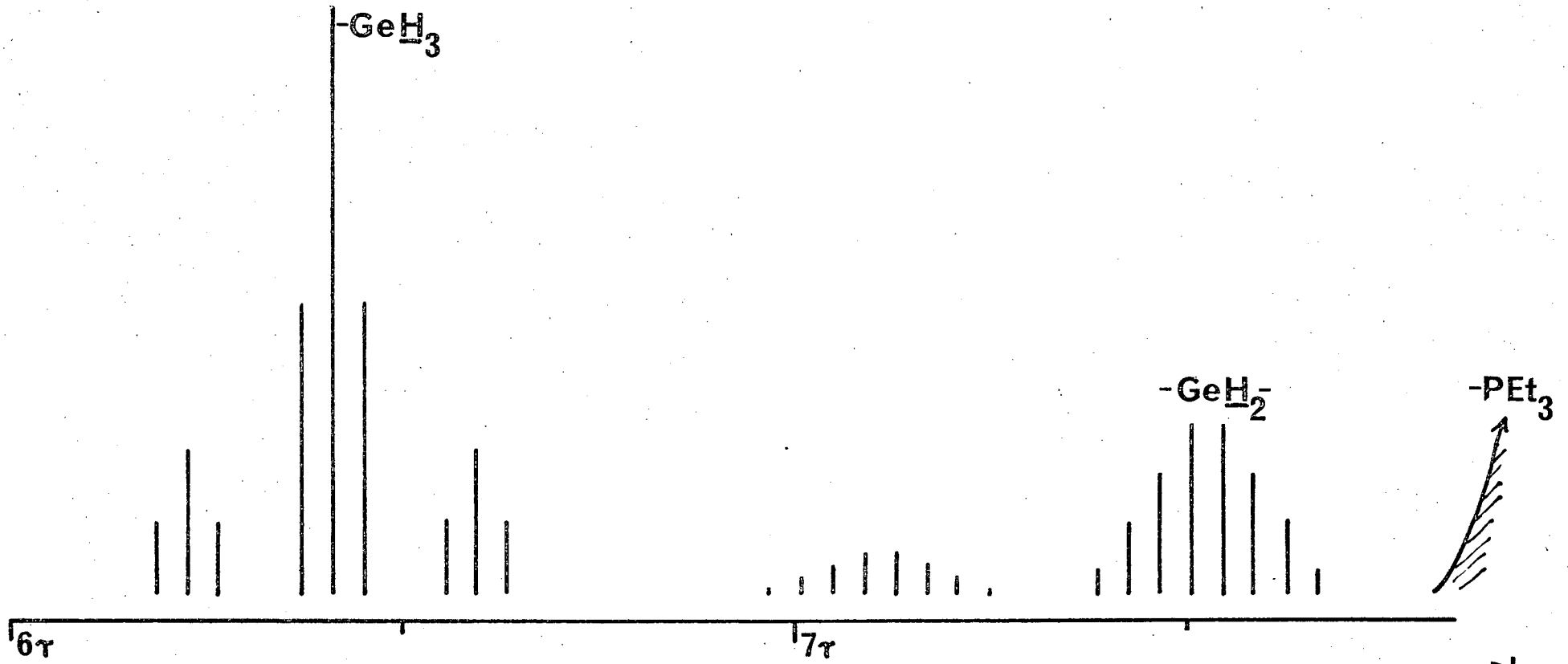
Parameters from the HM proton resonance spectra (M = Si, Ge) of trans-$XPt(PEt_3)_2Z$, where Z is a disilyl or digermyl species, measured relative to T.M.S.

Compound X	Pt	Z	τ ppm	J(HMPt) Hz	J(HMPtP) Hz	J(HMMH) Hz
Cl	Pt	$GeH_2.GeH_3$ [a]	7.51	84	8	4
Cl	Pt	$GeH_2.GeH_3$ [a]	6.39	37	-	4
I	Pt	$SiH_2.SiH_3$ [a]	7.07	n.o.	9.1	3.2
I	Pt	$SiH_2.SiH_3$ [a]	6.34	31.2	-	3.2
I	Pt	$SiHCl.SiH_3$ [b]	4.86	n.o.	11.5	3.1
I	Pt	$SiHCl.SiH_3$ [b]	6.08	27.5	-	3.1
I	Pt	$SiH_2.SiHCl_2$ [b]	6.73	35.4	8.8	2.8
I	Pt	$SiH_2.SiHCl_2$ [b]	3.97	n.o.	-	2.8
I	Pt	$SiHI.SiH_3$ [b]	n.o.	n.o.	n.o.	n.o.
I	Pt	$SiHI.SiH_3$ [b]	5.70	28.0	-	3.3

(a) measured in benzene at room temperature.

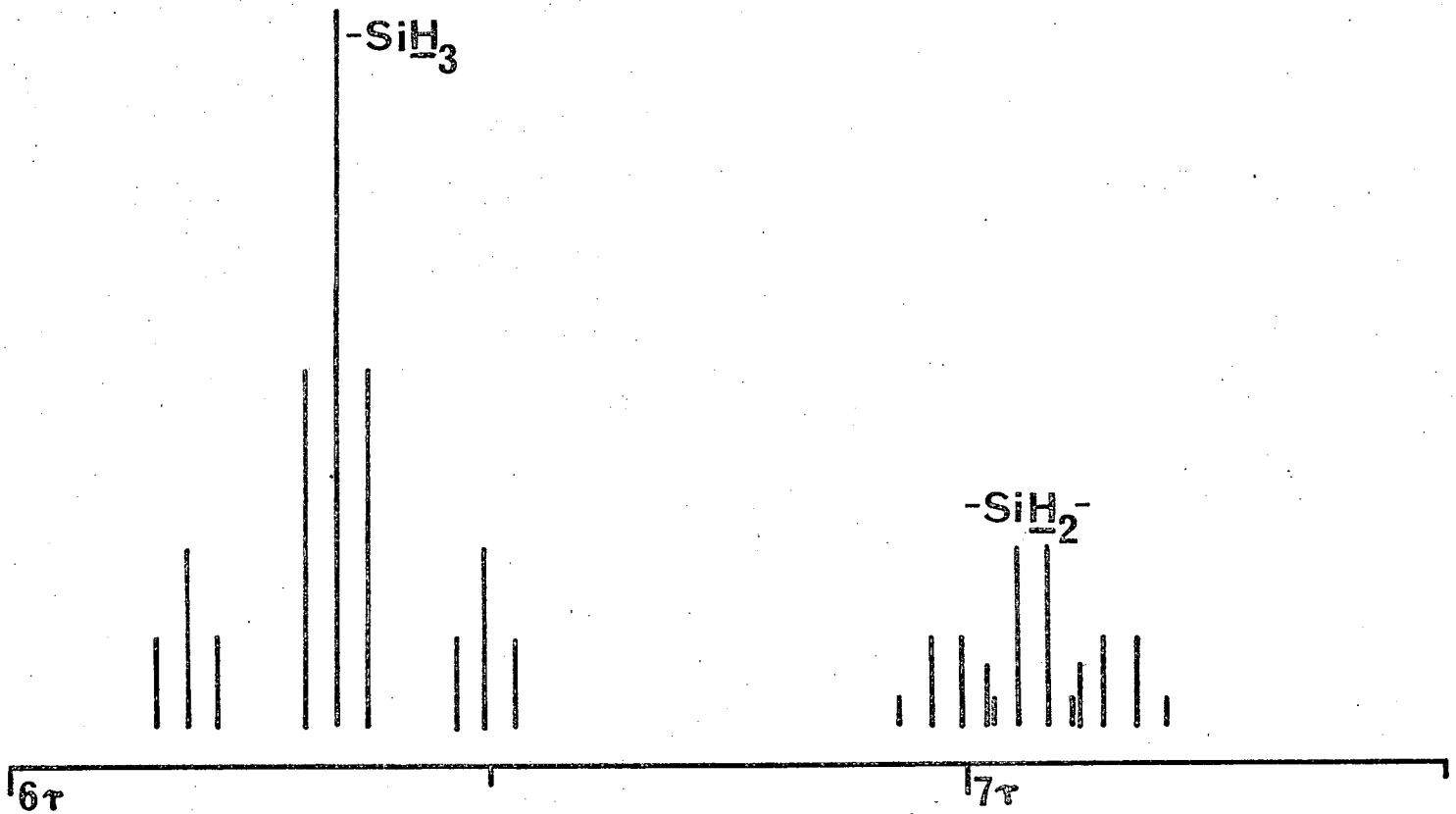
(b) measured in toluene at -15°.

Figure 4.1



N.M.R. spectrum of $ClPt(PEt_3)_2GeH_2GeH_3$

Figure 4.2



N.M.R. spectrum of $IPt(PEt_3)_2SiH_2SiH_3$

The n.m.r. spectrum which was used to identify the product, shown in Figure 4.2, is similar to that of the digermanyl compound. The n.m.r. parameters are also listed in Table 4.1. The disilanyl platinum compound as expected is more thermally stable than the digermanyl compound; a solution in benzene is stable for a few hours at room temperature. The reason for the difference in reaction of trans-$ClPt(PEt_3)_2H$ and trans-$IPt(PEt_3)_2H$ is not known.

Trans-$IPt(PEt_3)_2H$ reacts with Si_2H_5Cl and $SiH_3.SiHCl_2$ and the reactions are like that with Si_2H_6. The products of these reactions have been identified by their n.m.r. spectra at -15^o in toluene. Above -15^o they decompose and the triethylphosphine resonances slowly broaden as the HSi resonances disappear. Reaction between Ge_2H_5Cl and trans-$ClPt(PEt_3)_2H$ results only in dark brown decomposition products.

In the reaction with Si_2H_5Cl the silicon which is bound to chlorine becomes attached to platinum:

$$Si_2H_5Cl + \text{trans-}IPt(PEt_3)_2H \rightarrow \text{trans-}IPt(PEt_3)_2SiHCl.SiH_3 + H_2.$$

The reaction with $SiH_3.SiHCl_2$ gives the product in which the silicon attached to platinum is not bound to chlorine:

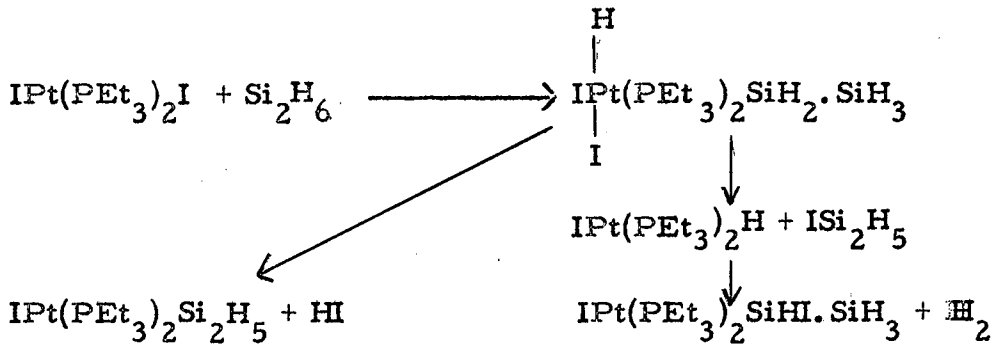
$$SiH_3.SiHCl_2 + \text{trans-}IPt(PEt_3)_2H \rightarrow \text{trans-}IPt(PEt_3)_2SiH_2.SiHCl_2 + H_2.$$

The resulting orientation of $SiH_3.SiH_2Cl$ when bound to platinum is consistent with electrophilic attack at platinum being important in the reaction. Assuming that such attack is important, the

expected orientation of $SiH_3.SiHCl_2$ when bound to platinum is the reverse of that observed. Steric hindrance may therefore be involved in the attack of the halogenated silicon in $SiH_3.SiHCl_2$.

These reactions may take place by oxidative addition of an MH bond followed by elimination of H_2 in the same manner as the reactions with monosilyl and monogermyl compounds discussed in Chapter I, though as before, no evidence has been obtained for any of the postulated intermediates. The reaction between Si_2H_6 and trans-$IPt(PEt_3)_2I$ was investigated because, by analogy with the monosilyl reactions, it was the reaction considered most likely to yield a six-coordinated product.

When Si_2H_6 is added to trans-$IPt(PEt_3)_2I$ reaction commences at -20° with some evolution of hydrogen. The n.m.r. spectrum of the reaction mixture indicates two products: trans-$IPt(PEt_3)_2SiH_2.SiH_3$ and trans-$IPt(PEt_3)_2SiHI.SiH_3$, but no six-coordinated intermediate is detected. If an intermediate is formed it must decompose fast. On warming the reaction mixture to 0° further reaction occurs, the resonances due to trans-$IPt(PEt_3)_2SiH_2.SiH_3$ disappear and some SiH_3I, SiH_4 and trans-$IPt(PEt_3)_2SiH_2I$ are formed. After ten minutes at room temperature the main products of reaction are trans-$IPt(PEt_3)_2SiH_2I$ and SiH_4. The initial products may possibly be explained in terms of a reaction scheme shown below:



The final products could be formed by reaction of H_2 or HI with the SiSi bond in the disilyl-platinum compounds

All the reactions discussed above are between equimolar amounts of reactants. They were also investigated using a two-fold excess of platinum hydride in an attempt to prepare a bis(platinum) compound, but the products were unchanged. However in a preliminary experiment, reaction of $ClH_2Si.SiH_2Cl$ with a two-fold excess of trans-$IPt(PEt_3)_2H$ gave a product with a symmetrical complex HSi n.m.r. spectrum possibly consistent with the formation of $Cl(PEt_3)_2Pt.SiHCl.SiHCl.Pt(PEt_3)_2Cl$.

CHAPTER V

SOME MORE SIX-COORDINATED PLATINUM COMPOUNDS AND INTERMEDIATES.

5.1 Introduction

Six-coordinated platinum compounds are formed by the addition of an M-H bond to trans-$(PEt_3)_2PtI_2$ as described in Chapter II. Further six-coordinated compounds, of a rather different nature from $I_2Pt(PEt_3)_2H.MH_2X$, are formed by reaction of germyl chloride with platinum silyl and platinum germyl compounds. The use of n.m.r. spectroscopy in the identification of these compounds is described in this Chapter together with postulated mechanisms for the reactions.

5.2 The reaction of germyl chloride with trans-$ClPt(PEt_3)_2GeH_2Cl$.

Germyl chloride reacts with an equimolar quantity of trans-hydridochlorobis(triethylphosphine) platinum(II) as described in Chapter I. The product of the reaction, trans-$ClPt(PEt_3)_2GeH_2Cl$, has a characteristic n.m.r. spectrum which is similar to that shown in Figure 1.2. When an excess of GeH_3Cl is used, further reaction occurs[88] and some new peaks appear in the n.m.r. spectrum, shown in Figures 5.1 and 5.2. The new peaks at about 4.7τ were attributed to $-GeH_2Cl$ derivatives of Pt, and those at about 21τ to Pt<u>H</u>. The resonance centred on 4.7τ is complicated but it is possible to distinguish two strong triplets (P and Q) and their

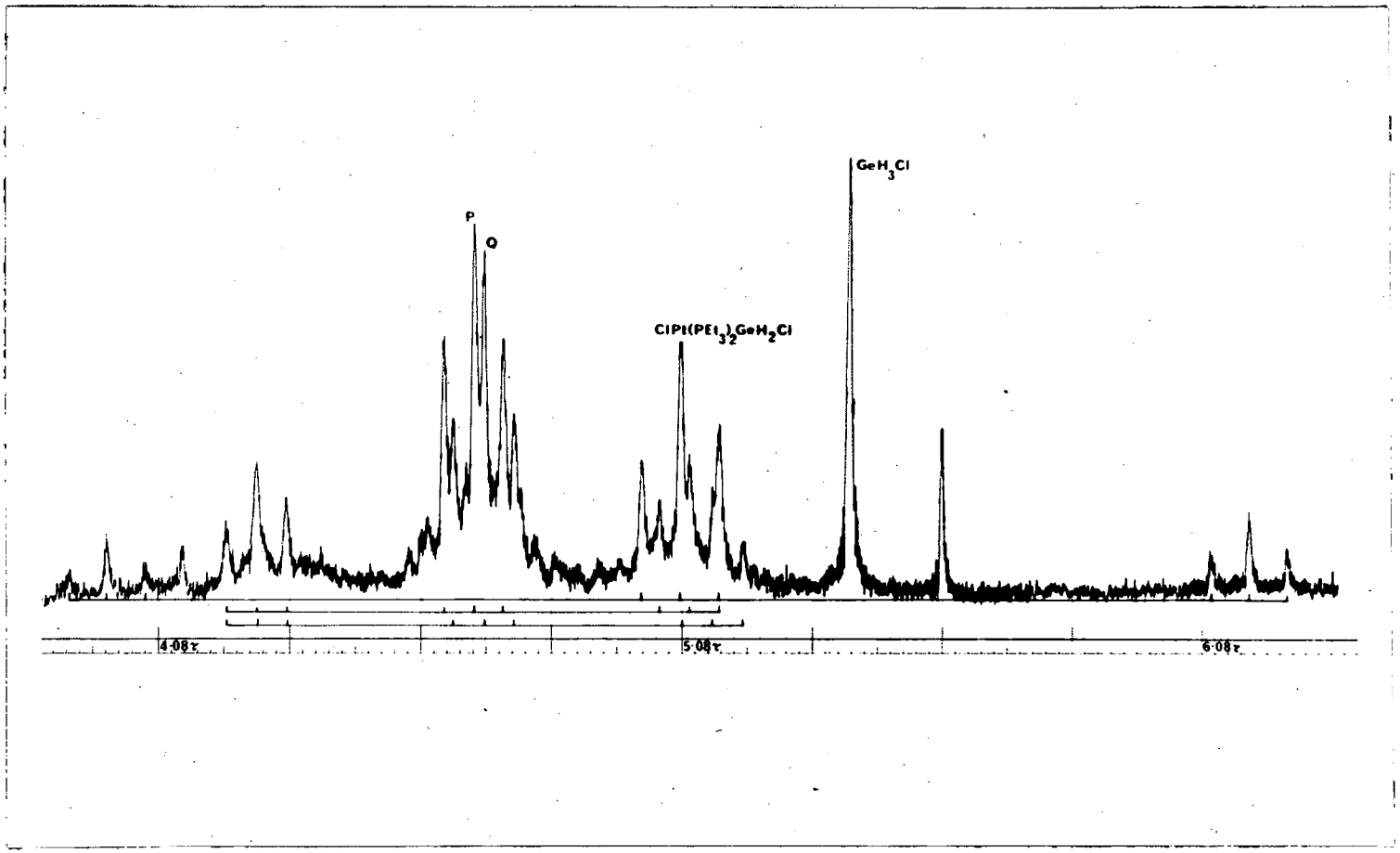


Figure 5.1

Proton n.m.r. spectrum of the products of reaction between trans-$ClPt(PEt_3)_2H$ and $3GeH_3Cl$.

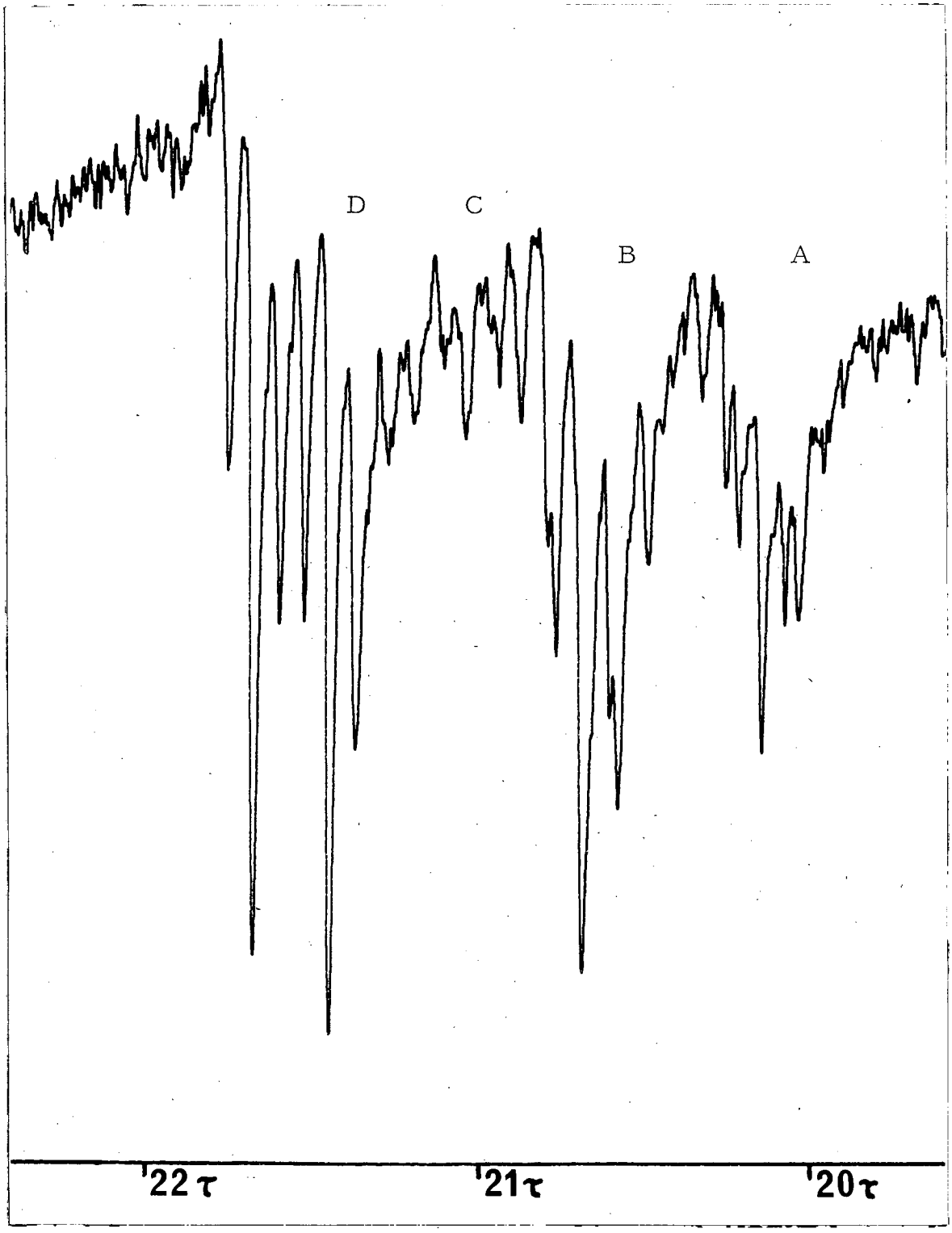


Figure 5.2

High field proton n.m.r. spectrum of the products of reaction between trans-$ClPt(PEt_3)_2H$ and $3GeH_3Cl$.

associated Pt^{195} side-bands. The magnitudes of the hydrogen-platinum coupling constants, J(HGePt) are 83.0 Hz for P and 87.0 Hz for Q. Both these values are much smaller than in trans-$ClPt(PEt_3)_2GeH_2Cl$, where J(HGePt) is 218.8 Hz. By comparison with the results obtained for $I_2Pt(PEt_3)_2H.GeH_2I$ the values of the coupling constants suggested that the new peaks were possibly due to six-coordinated platinum compounds. The triplet pattern of the peaks indicated that the compounds had two equivalent phosphines, probably trans to each other.

The platinum hydride resonance appeared to be composed of four sets of peaks: a triplet of triplets (A), a triplet of triplets (B), a doublet of triplets (C) and another doublet of doublets (D). The separations attributed to couplings were confirmed as such, because they were the same when measured at 100 MHz and 60 MHz, and the triplet structure of the peaks again suggested trans phosphines. The relative intensities of the platinum hydride resonances A, B, C, D and the germanium hydride resonances P, Q depended on the molar ratio of GeH_3Cl : $ClPt(PEt_3)_2H$. When the ratio was 2:1, the intensity of B was greater than that of A, C and D; the intensity of Q was greater than that of P. When the ratio was increased to 3:1, the intensity of B and Q decreased, the intensity of A, D and P increased and that of C remained very

low. As the ratio was further increased to 5:1, C became more intense and A, B and Q decreased in intensity relative to D and P. This series of experiments showed that the intensities of the resonances A, B, C, D varied independantly with the change in the amounts of the reactants, and therefore suggested that each resonance A, B, C and D was associated with a different product. In view of the ways in which their intensities varied together, it was possible that there was a connection between Q and B, and between P and D.

With the aid of this information, together with more data obtained from spin decoupling experiments, the peaks were assigned to the compounds shown below, which are dealt with in order of their appearance with increasing amounts of GeH_3Cl. The possible mechanism of the reaction is discussed later.

Figure 5.3

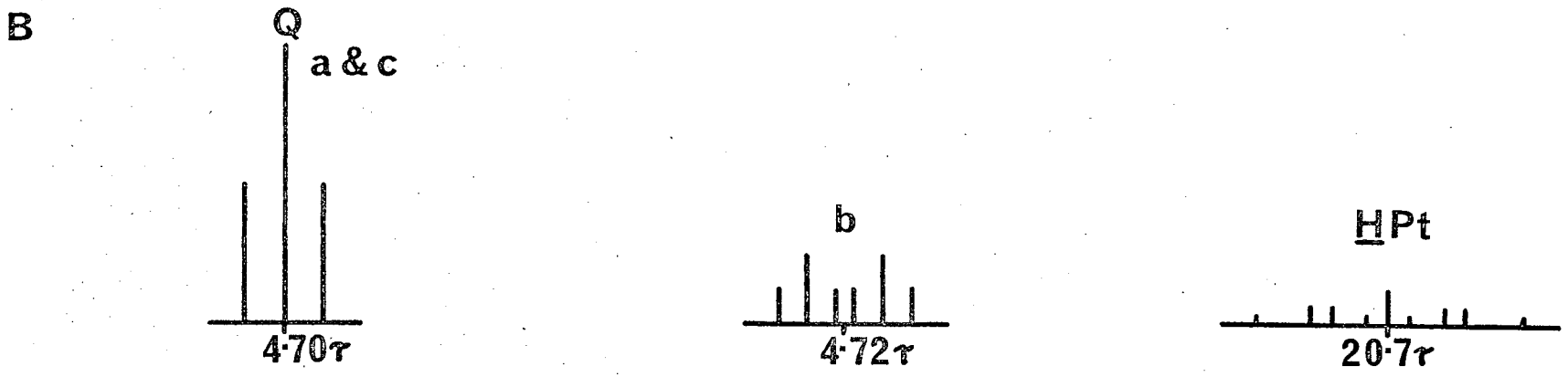
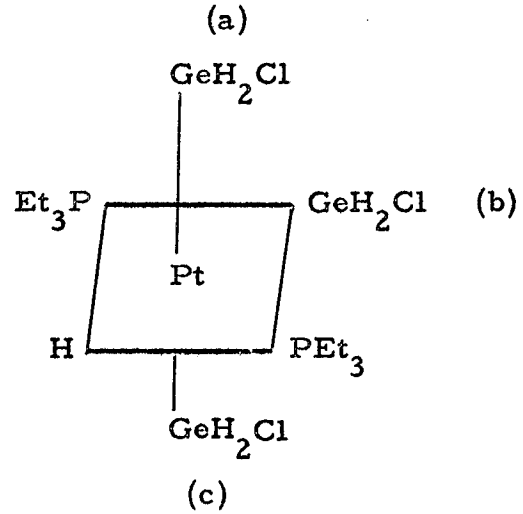


Table 5.1

Proton	τ ppm	J(HPt) Hz	J(HP) Hz	J(HPtGeH) Hz
HPt	20.70	733	8.0	11.0
a and c	4.70	87.0	5.8	-
b	4.72	n.o.	4.0	11

B



The n.m.r. spectrum of B is represented in Figure 5.3 and the associated parameters are shown in Table 5.1. The triplet Q is assigned to the two equivalent -GeH_2Cl groups (a) and (c) cis to Pt-H. The Pt<u>H</u> resonance is assumed to be split into a triplet by the two phosphorous atoms, and into a further triplet by the -GeH_2Cl group (b), trans to platinum hydrogen. The resonance assigned to -GeH_2Cl (b) is split into a doublet, also consistent with coupling to Pt<u>H</u>. This trans-<u>H</u>PtGe<u>H</u>$_2$Cl coupling was confirmed when irradiation at the resonance frequency of -GeH_2Cl (b) caused some collapse of the Pt<u>H</u> resonance. Coupling was only observed between protons in the groups (a), (b), (c) and Pt<u>H</u> when two groups were mutually trans.

Figure 5.4

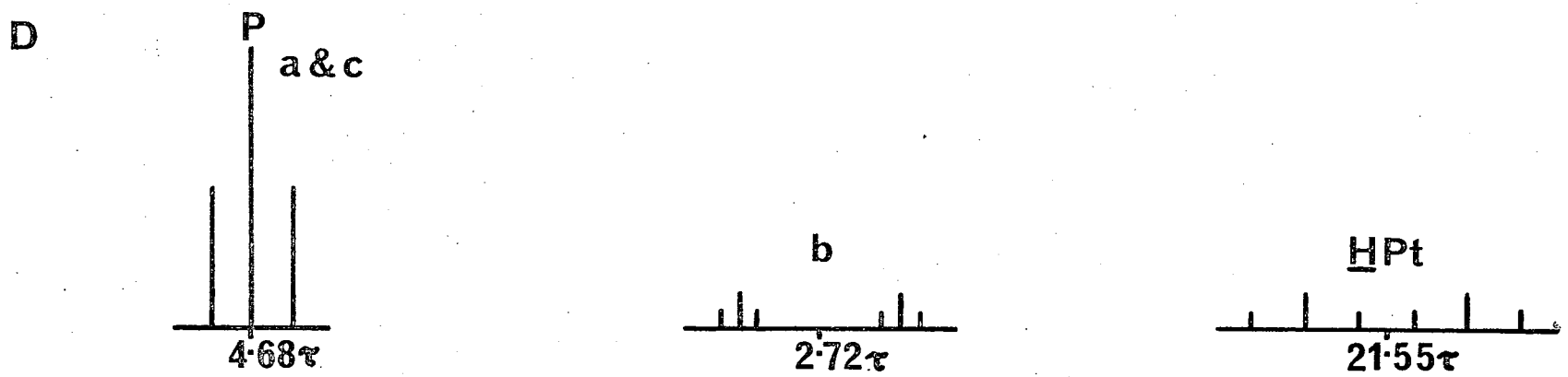
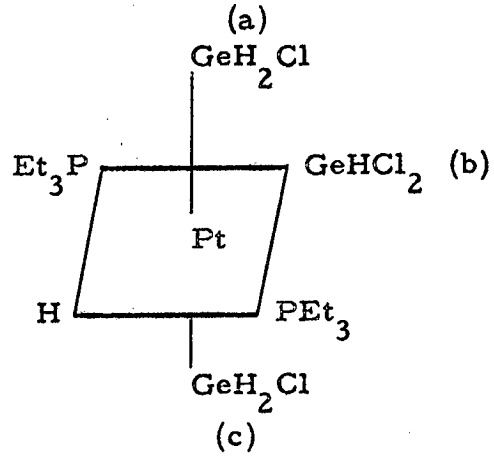


Table 5.2

Proton	T ppm	J(HPt) Hz	J(HP) Hz	J(HPtGeH) Hz
HPt	21.55	751	7.7	23.0
a and c	4.68	83.0	5.8	-
b	2.72	143.5	2.7	23.0

D



The n.m.r. spectrum of D is shown in Figure 5.4 and the associated parameters are shown in Table 5.2. The triplet P is assigned to the two equivalent $-GeH_2Cl$ groups (a) and (c). The Pt<u>H</u> resonance is a doublet of triplets. The doublet splitting remained a mystery for some time until it was discovered that irradiation at the frequency associated with the solvent (benzene) resonance caused some collapse of the Pt<u>H</u> resonance. The region of the spectrum under the solvent was examined using deuterobenzene as solvent instead of benzene. Only one peak (a triplet) was found but four peaks assigned to Pt^{195} side-bands indicated that there was another triplet underneath the solvent resonance. The estimated separation of the two main triplets was exactly the same as the doublet separation in the Pt<u>H</u> resonance, confirming that this splitting was due to trans-$\underline{H}PtGe\underline{H}Cl_2$ coupling. In another experiment with a more concentrated solution of the platinum compound, the chemical shift of $-Ge\underline{H}Cl_2$ (b) was shifted up-field relative to the solvent and both main triplets were observed. As for B no cis coupling was observed between $-GeH_2Cl$ (a), (c) and Pt<u>H</u>.

Figure 5.5

A

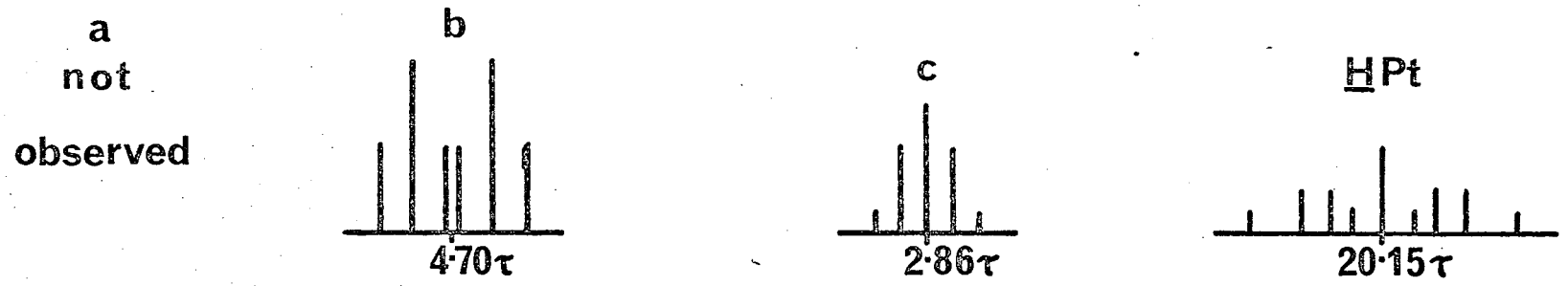
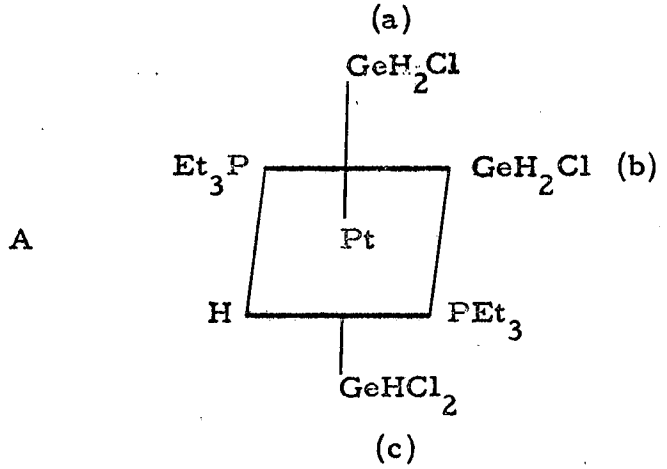


Table 5.3

Proton	τ ppm	J(HPt) Hz	J(HP) Hz	J(HPtGeH) Hz	J(HGePtGeH) Hz
HPt	20.15	734	7.0	11.0	-
a	[4.84]	n.o	n.o.	-	~3.5
b	4.70	n.o	4.5	11.0	-
c	2.86	166	~3.5	-	~3.5

Numbers in brackets are deduced from frequencies for spin decoupling; numbers underlined are deduced from frequencies in other resonances.



A

As shown in the structure drawn above, A is an isomer of D. The n.m.r. spectrum of A is represented in Figure 5.5 and the associated parameters are shown in Table 5.3. The Pt<u>H</u> resonance is very similar in pattern to that of B, and the trans-<u>H</u>PtGe<u>H</u>$_2$Cl coupling was similarly confirmed when irradiation at the resonance frequency of -Ge<u>H</u>$_2$Cl caused some collapse of the Pt<u>H</u> resonance. Some of the peaks in the -GeH$_2$Cl (b) resonance were observed, but no peaks could be assigned to -GeH$_2$Cl (a), cis to PtH, indicating that they must have been hidden underneath other peaks in that region. The resonance due to -Ge<u>H</u>Cl$_2$(c) was identified as a triplet of triplets, using deuterobenzene as solvent. Initially the main -Ge<u>H</u>Cl$_2$ (c) resonance was not observed and only the Pt^{195} satellites were visible. By using a more concentrated solution of the platinum compound the chemical shift of the -Ge<u>H</u>Cl$_2$ proton (c) was shifted upfield relative to that of the solvent and the main resonance became visible on the side of the solvent resonance. Irradiation at a

frequency estimated for the -GeH_2Cl (a) resonance appeared to cause some collapse of the -$GeHCl_2$ (c) resonance. The triplet splitting pattern was therefore tentatively assigned to coupling with the two phosphines and with the protons -$Ge\underline{H}_2Cl$ (a) trans to -$GeHCl_2$ (c). These two couplings are of approximately the same magnitude and it is not possible to determine either coupling constant accurately. The long range coupling J($\underline{H}$GePtGe$\underline{H}$) was also observed in the n. m. r. spectrum associated with C in which the evidence for the coupling was stronger.

Figure 5.6

C

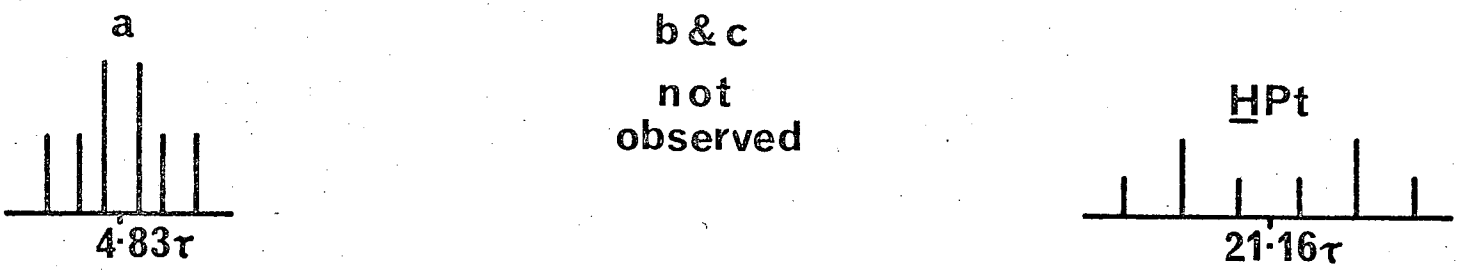
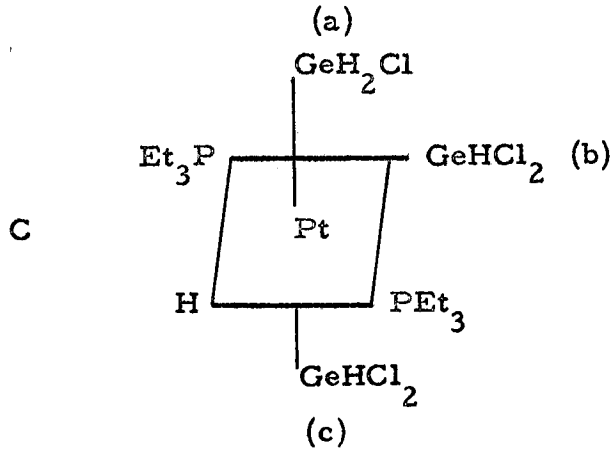


Table 5.4

Proton	τ ppm	J(HPt) Hz	J(HP) Hz	J(HPtGeH) Hz	J(HGePtGeH) Hz
HPt	21.16	752	7.5	23.0	-
a	4.83	87.0	7.5	-	4.5
b	[2.80]	n.o	n.o	23.0	-
c	[2.80]	n.o	n.o	n.o	4.5

Numbers in brackets are deduced from frequencies for spin decoupling; numbers underlined are deduced from frequencies in other resonances.



The resonance associated with this compound (represented in Figure 5.6) was only of significant intensity when a large excess of germyl chloride was reacted with trans-$ClPt(PEt_3)_2H$. However, when GeH_2Cl_2 was reacted with trans-$ClPt(PEt_3)_2GeH_2Cl$, this resonance was the strongest in the spectrum and could be used for assignment of the peaks. The Pt<u>H</u> resonance is similar to that of D and the doublet splitting was similarly confirmed as J(trans-<u>H</u>PtGe<u>H</u>Cl_2) using spin decoupling. The resonance assigned to the -Ge<u>H</u>$_2$Cl group (a), trans to -$GeHCl_2$ (c) is a doublet of triplets. Irradiation at the estimated -Ge<u>H</u>Cl_2 (c) resonance frequency showed that the doublet splitting was due to coupling with the -Ge<u>H</u>Cl_2 (c) proton, because complete collapse into one triplet was observed.

The n.m.r. spectrum of the products of the reaction between GeH_2Cl_2 and trans-$ClPt(PEt_3)_2GeH_2Cl$ showed evidence for another compound. There was a doublet of triplets in the Pt<u>H</u> region and one triplet at 2.2τ. The n.m.r.

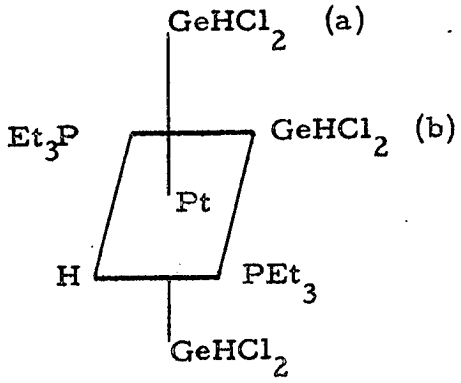
parameters are listed in the Table below:

Table 5.5

Resonance	τ (p.p.m.)	J(HPtP) Hz	J(HPtGeH) Hz.
PtH	20.96	7.5	23
$PtGeHCl_2$ (a)	2.22	5.5	-

These values are tentatively assigned to a compound having the structure:

E

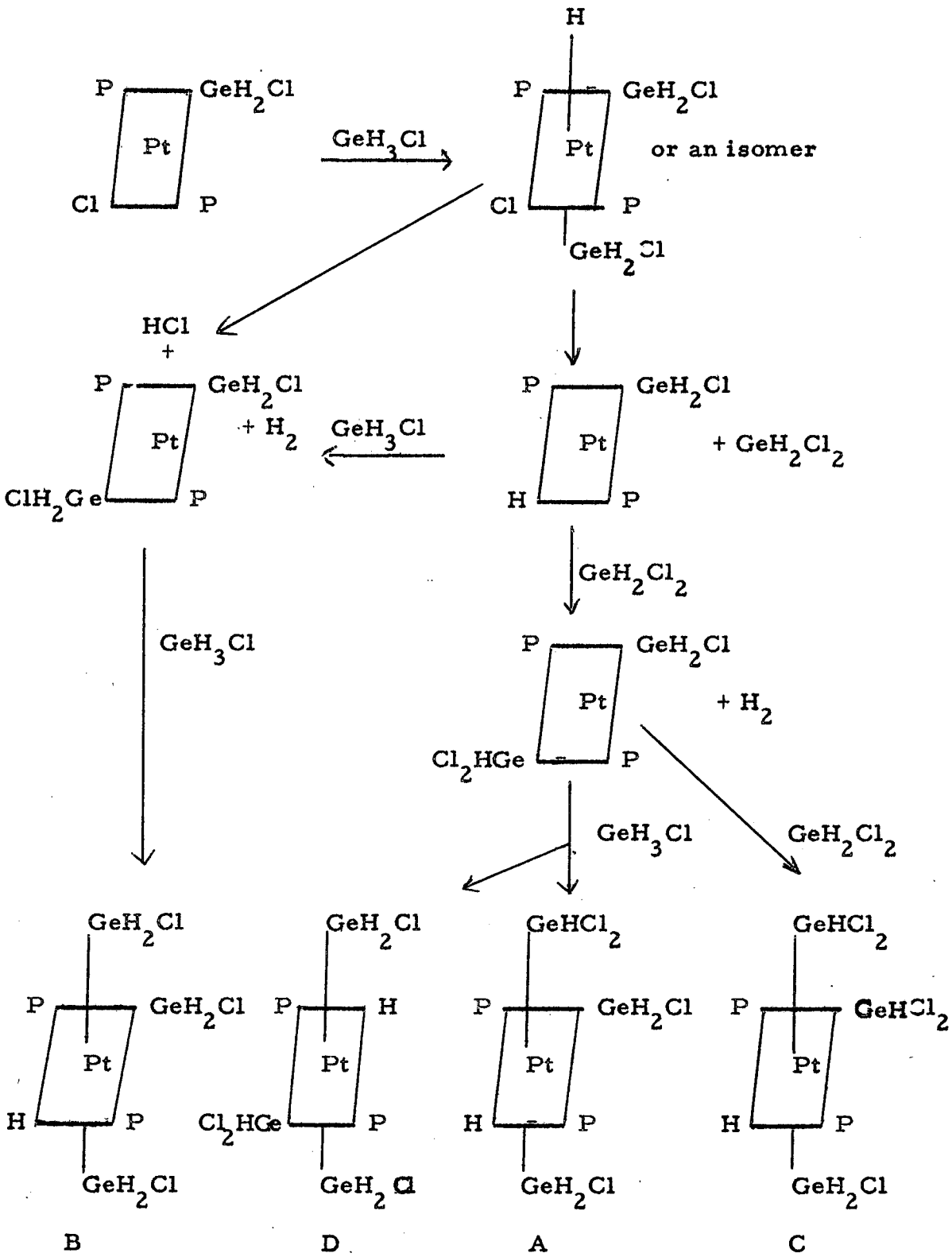


(a)

The compounds A, B, C, D and E may have been formed by a series of addition reactions to four-coordinated platinum(II) followed by eliminations from the six-coordinated platinum(IV) intermediates formed. A possible reaction scheme is drawn out on the next page. The reactions in which hydrogen is evolved are assumed to occur by a mechanism similar to that of the preparative reaction, described in Chapter I. No direct evidence for any of the postulated intermediates has been obtained, perhaps because the final addition of a Ge-H bond to form a six-coordinated product is fast compared with the formation of intermediates. The postulated mechanism is supported by the fact that hydrogen and HCl have been isolated

Figure 5.7 Reaction of germyl chloride with $Cl(PEt_3)_2H$: postulated mechanism.

$$trans\text{-}ClPt(PEt_3)_2H + GeH_3Cl \longrightarrow trans\text{-}ClPt(PEt_3)_2GeH_2Cl + H_2$$



from the reaction products. Dichlorogermane may have reacted as did GeH_3Cl with trans-$ClPt(PEt_3)_2GeH_2Cl$, but would have then formed products with Cl substituted for some of the hydrogens on germanium. Thus the most likely products from this reaction scheme would be C and E; these are observed. It is possible that some -$GeCl_3$ derivatives may have been formed, but these would not have been detected in the n.m.r. spectrum. Some six-coordinated Pt(IV)$GeCl_3$ complexes have been prepared by Urry[62], including $(PPh_3)_2PtCl_2(GeCl_3)_2$ but the preparative reactions were carried out in concentrated hydrochloric acid and the mechanism probably involved attack of $GeCl_3^-$.

As mentioned previously in Chapter II, the reaction of trans-$ClPt(PEt_3)_2Cl$ with germyl chloride does not follow the same course as the reaction with a silyl halide. The n.m.r. spectrum of the former shows peaks in the same positions as A, B, C and D, possibly due to the slow formation of trans-$ClPt(PEt_3)_2GeH_2Cl$ which would react as shown in the reaction scheme above to form the six-coordinated tris-(germyl)-platinum hydrides.

Glockling has isolated some octahedral platinum substituted tin compounds[56], which may have been formed in a similar manner.

$$(diphos)PtCl_2 + \text{excess } Me_3SnH \rightarrow (diphos)PtH.Cl(SnMe_3)_2 + Me_3SnCl$$

$$\uparrow\downarrow$$

$$(diphos)PtH(SnMe_3)_3 \xleftarrow{\text{x. s. } Me_3SnH} (diphos)Pt.Cl.SnMe_3 + Me_3SnH.$$

5.3 The reaction of germyl chloride with trans-$ClPt(PEt_3)_2SiH_2Cl$.

Germyl chloride also reacts with an equimolar quantity of $ClPt(PEt_3)_2SiH_2Cl$[86]. The n.m.r. spectrum of the reaction mixture is shown in Figure 5.8 and indicates that the products of the reactions are: SiH_3Cl, unreacted trans-$ClPt(PEt_3)_2SiH_2Cl$, H_2, SiH_2Cl_2, trans-$ClPt(PEt_3)_2GeH_2Cl$ and $HPt(PEt_3)_2(GeH_2Cl)_3$. The reaction seemed to be complicated, but could be considered, in part, as a silyl-germyl exchange:

$$GeH_3Cl + ClPt(PEt_3)_2SiH_2Cl \longrightarrow ClPt(PEt_3)_2GeH_2Cl + SiH_3Cl.$$

Silyl-germyl exchange reactions have been investigated in some detail[83,84,85].

$$\text{e.g. } GeH_3F + SiH_3NCO \longrightarrow SiH_3F + GeH_3NCO.$$

These reactions involve no change in the number of hydrogens attached to Si or Ge, and hence differ from the reaction on platinum, which formally involves a PtSi/GeH exchange. The production of the six-coordinated platinum hydride was unusual because it was prepared as a pure compound, whereas all the preparations involving germyl chloride and trans-$ClPt(PEt_3)_2H$ resulted in a mixture of six-coordinated platinum hydrides. The results can be clarified by consideration of a possible reaction scheme, the first step being addition of a Ge-H bond to platinum.

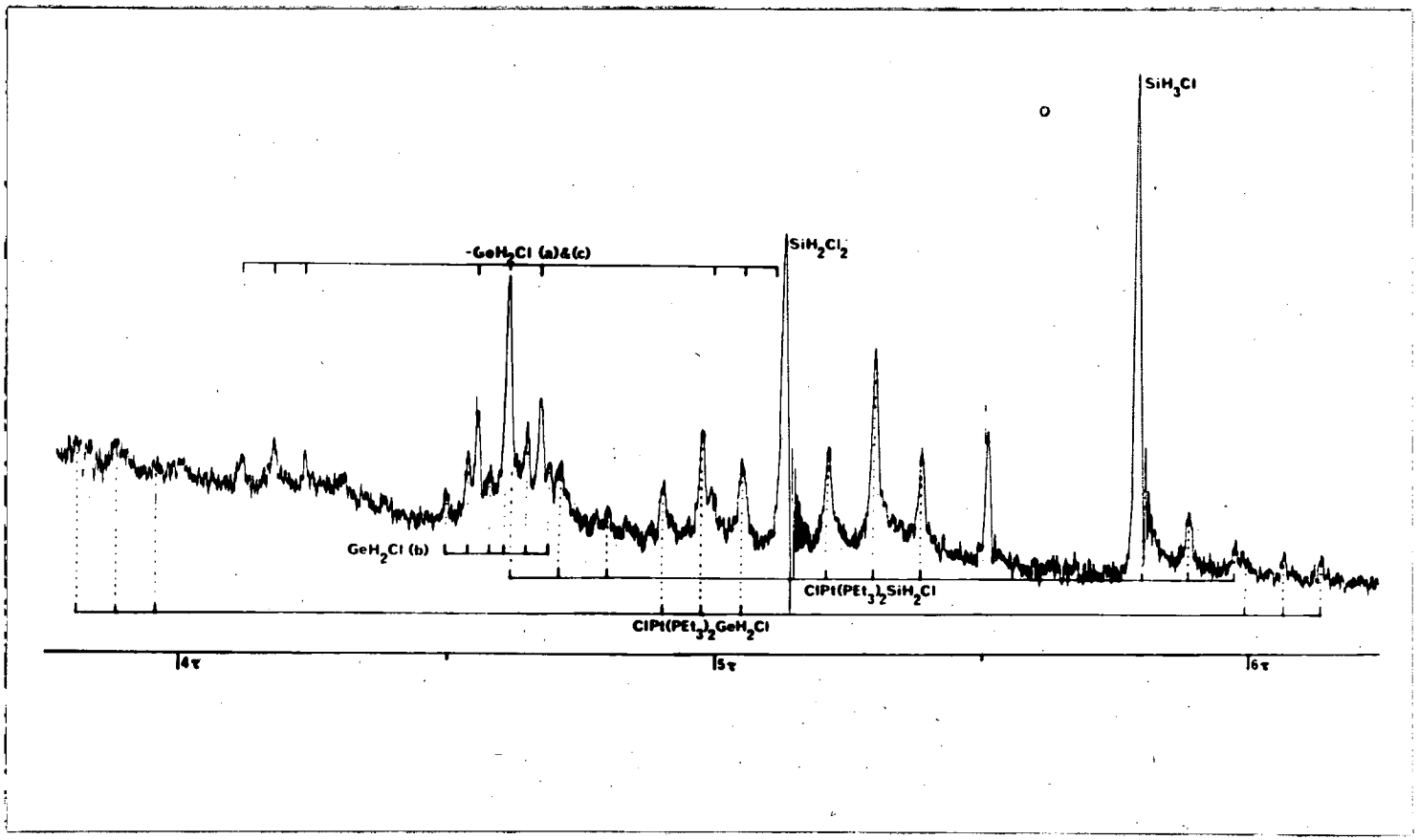
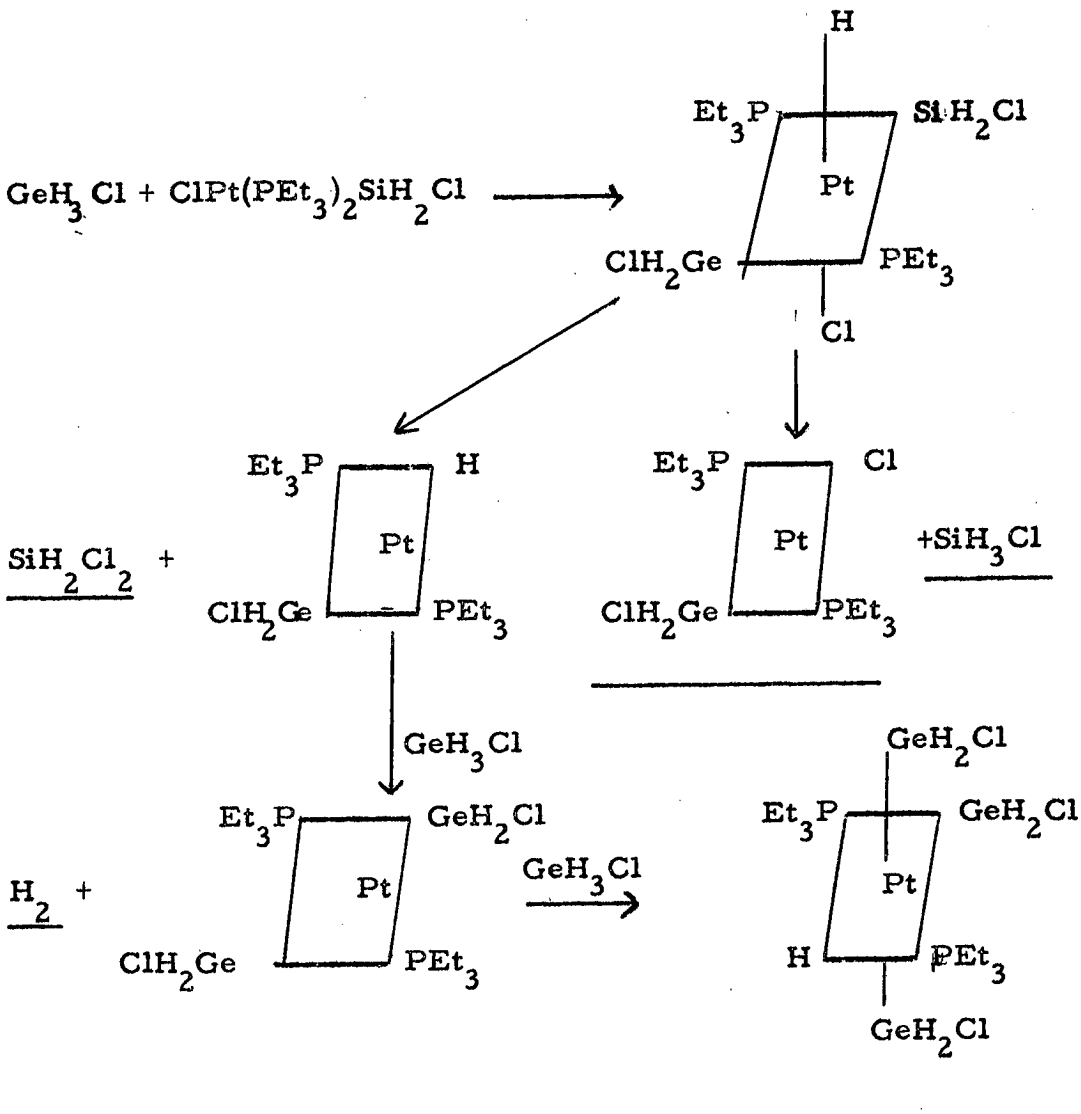
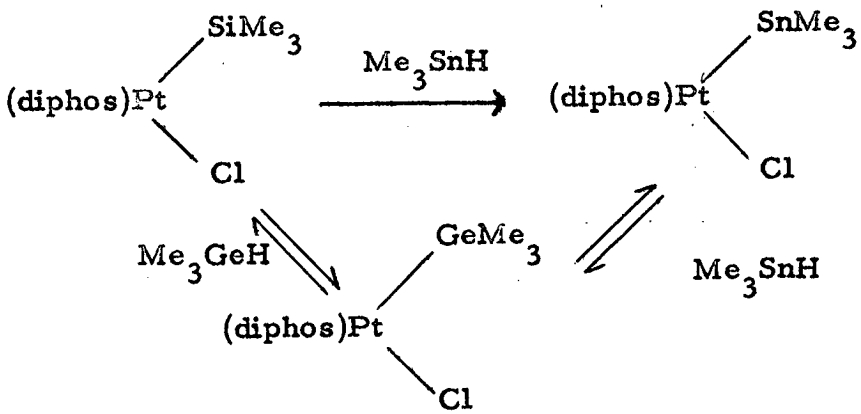


Figure 5.8

Proton n.m.r. spectrum of the products of reaction between trans-$ClPt(PEt_3)_2SiH_2Cl$ and GeH_3Cl; $-GeH_2Cl$ (a), (b) and (c) are the same as in Figure 5.3.



Again, no direct evidence has been obtained for any of the intermediates. Glockling has since reported similar exchange reactions[52]:



The products also react further as shown previously, to form six-coordinated tris-(trimethyltin)-platinum hydrides.

5.4 Some related reactions with iodide derivatives.

All the reactions mentioned above involved chloride derivatives of platinum and M. The reactions were investigated using iodide derivatives, but interpretation using n.m.r. spectroscopy was more difficult because some precipitation occurred. Thus the n.m.r. spectrum of a reaction between $2GeH_3I$ and trans-$IPt(PEt_3)_2H$ indicated a mixture of slightly soluble products, including one weak set of triplets with J(HGePt) = 67.5 Hz, which was probably due to a six-coordinated platinum compound. The spectrum was too weak to observe a PtH resonance, but the infrared spectrum of the mixture of products showed a band at 2198 cm^{-1}, assigned to a platinum-hydrogen stretching vibration.

In the reaction of GeH_3I with $IPt(PEt_3)_2SiH_2I$, a precipitate was formed in the same manner, but some silicon/germanium exchange did occur because SiH_3I was detected among the products. The n.m.r. spectrum of the reaction products showed a mixture of slightly soluble compounds, one of which was the same as the possible six-coordinated species produced in the reaction of $2GeH_3I$ with $IPt(PEt_3)_2H$. There was no change when the six-coordinated adduct $I_2Pt(PEt_3)_2H.SiH_2I$ was treated with GeH_3I, showing that four-coordinated

platinum is a necessary requirement for such exchange reactions.

5.5 Some thermodynamic considerations.

The reactions which have been discussed in this chapter demonstrate the great facility with which Ge-H bonds can be added across four-coordinated platinum(II). As mentioned in Chapter II, silyl halides do not react in the same manner. Silyl chloride reacts only very slowly with trans-$ClPt(PEt_3)_2SiH_2Cl$ forming a two phase system after one week at room temperature. This behaviour has not been explained, but it is possible that the ease of addition of Ge-H compared with Si-H in the above system could be attributed to thermodynamic factors. The bond between germanium and a transition metal is thought to be stronger than that between silicon and a transition metal[2], and as mentioned in the introduction the GeH bond energy is less than that of the SiH bond. Thus, assuming that the other bonds to platinum remain relatively unchanged, the addition of a Ge-H bond to Pt will be more energetically favourable than the addition of Si-H. The exchange reaction demonstrates this:

$$GeH_3Cl + ClPt(PEt_3)_2SiH_2Cl \longrightarrow ClPt(PEt_3)_2GeH_2Cl + SiH_3Cl.$$

However, contribution from kinetic factors cannot be discounted.

CHAPTER VI

SOME CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

Much of the discussion in this thesis has been concerned with the interpretation of various reactions in terms of intermediates containing six-coordinated platinum. The evidence upon which this interpretation is based comes from the nature of the reaction products, the products reported from similar reactions of related compounds, and the isolation of six-coordinated compounds, some of which behave in a similar fashion to the postulated intermediates. The possibility that some of these reactions occur by a different mechanism has been considered but on balance it seems likely that the six-coordinated intermediates are formed although they must decompose rapidly.

Some factors which may influence the rapid elimination of two ligands bound to six-coordinated platinum(IV) have been discussed. One of these factors was the strength of the MX bond formed by elimination of a silyl or germyl group and X from platinum(IV). None of the postulated intermediates containing chlorine bound to platinum has been detected, suggesting that such intermediates might be inherently unstable with respect to elimination of an M-Cl species. The possibility of forming six-coordinated compounds with bromine bound to platinum has not been investigated and would provide one line of

future research. On the basis of the argument presented above, treatment of trans-$BrPt(PEt_3)_2Br$ with SiH_3Cl may give a six-coordinated compound which is intermediate in stability towards elimination, between $I_2Pt(PEt_3)_2H.SiH_2Cl$ and $Cl_2Pt(PEt_3)_2H.SiH_2Cl$.

The rate of the reaction between SiH_3Cl and trans-$XPt(PEt_3)_2X$ (X = I, Cl) has been discussed in terms of electrophilic attack at platinum. The experiment with X = Br would provide a test of this hypothesis which could be investigated further by a study of the rate of reaction of SiH_3Cl with a series of platinum compounds where X = CN, Me, Ph, alkyl etc. The information gained from rate studies might also give some indication of the mechanism of reaction. A study of the rate of exchange of Et_3P with trans-$XPt(PEt_3)_2SiH_2X$ might similarly indicate a possible mechanism for the phosphine exchange.

In addition to these rate studes there are other lines of research, leading out of results presented in the thesis, where more work is needed. The reaction of SiH_3Cl with trans-$ClPd(PEt_3)_2Cl$ is of some interest because it appears to proceed via formation of a six-coordinated intermediate. Formation of such intermediates with palladium has previously been considered unlikely[59]. A detailed study of the reactions between MH_3X and trans-$YPd(PEt_3)_2Y$ or trans-$ClPd(PEt_3)_2H$[90], if necessary at low temperatures, might lead to detection of a six-coordinated compound.

The study of some platinum substituted disilyl and digermyl compounds, reported in Chapter V, was only a preliminary series of experiments. Amongst much work required to complete the study there are in particular two speculative results mentioned in Chapter V which might be clarified by further experimentation. In the reaction of Si_2H_6 with trans-$IPt(PEt_3)_2I$, it appeared that the Si-Si bond in trans-$IPt(PEt_3)_2SiHISiH_3$ was cleaved by HI or H_2. Some further experiments, perhaps with the most stable derivative trans-$IPt(PEt_3)_2Si_2H_5$ and hydrogen halides or hydrogen, might provide more evidence of such a reaction. The nature of the possible bis(platinum) disilyl compound $[Cl(PEt_3)_2PtSiHCl]_2$ could be confirmed by an analysis of the n.m.r. spectrum if it proved impossible to isolate the compound from solution.

The problem of the two-phase systems which have appeared in several of the reactions remains unsolved. Conductivity and molecular weight determinations might give some indication of the nature of the system.

The suggestions for future work, which have been mentioned above, are some examples of points arising from work described in the thesis. There are other reactions with different systems which could be investigated including, in particular, the reactions of bis(silyl) or bis(germyl) species such as $(SiH_3)_2O$ with platinum hydrides and the reactions of

silyl or germyl compounds with olefinic derivatives of platinum. However, all these suggestions for future research have been concerned only with platinum. A relatively large number of transition metals form complexes with organosilanes and organogermanes but, as shown in the introduction, few silicon and germanium hydride derivatives of transition metals are known and there remains a large field of potentially interesting chemistry which has been completely unexplored. One of the conclusions which may be drawn from this thesis is that a study of hydride derivatives compliments the study of organo derivatives and may provide additional information relevant to the understanding of the chemistry of silicon and germanium complexes of transition metals.

CHAPTER VII

EXPERIMENTAL.

7.1 Experimental Methods

Volatile compounds were manipulated in a conventional Pyrex glass vacuum system. Quantities of condensible materials were measured in a calibrated volume using a glass spiral gauge to measure pressures. Volumes of non-condensible gases were measured using a Toepler pump. Involatile air-sensitive solids were handled under dry nitrogen in an evacuable glove-box or a polythene bag and reactions were normally carried out in all-glass break-seal ampoules.

Infrared spectra were recorded using a Perkin-Elmer 457 spectrometer. For high resolution spectra or for low frequency spectra down to 200 cm^{-1} a Perkin-Elmer 225 spectrometer was used. Vapour phase and solution spectra were recorded in the normal manner. Nujol mull spectra were recorded using CsI plates held in a sealed container. The nujol was carefully dried with sodium wire. Raman spectra were run on a Cary 81 laser Raman spectrometer, using finely powdered solid samples. Proton n.m.r. spectra were sometimes recorded on a Perkin-Elmer R10 spectrometer, operating at 60 MHz, but a Varian Associates H.A. 100 spectrometer operating at 100 MHz was used most

often. In the normal field or frequency sweep H.A. modes of operation the range of the H.A. 100 spectrometer is limited by the range of the manual oscillator (1500 - 3,500 Hz) and the range of the swept oscillator (2,500 - 3,500 Hz) to 10T (1000 Hz) to high-field of the lock and to 20T (2,000 Hz) to low-field of the lock. Thus transition metal hydride resonances with a chemical shift above 20T are beyond the range of normal operation of the instrument because the internal standard having the highest practical chemical shift is T.M.S. (10T). The high-field range of the spectrometer was extended by using the frequency sweep mode while locking on the first lower side-band of the T.M.S. main resonance. The recorded spectrum was then upside-down and back to front and the high-field limit was 30T, 2000 Hz above the lock. It was found that the exciting power could be increased by 10 d.B. without saturation, thus improving the sensitivity for detection of any high-field resonance though the phase was difficult to adjust as shown in Figure 5.2.

Analysis for C, H, P and halogen was carried out by A. Bernhardt. Analysis for C and H only was carried out using a Perkin-Elmer 240 Elemental Analyser in this Department. Only selected representative compounds were analysed so that the spectroscopic assignments could be confirmed. Attempts to record Mass Spectra resulted only in peaks due to decomposition products.

7.2 Starting Materials

Compound	Method	Reference
SiH_4	$SiCl_4 + LiAlH_4$	91
SiD_4	$SiCl_4 + LiAlD_4$	91
Si_2H_6	$Si_2Cl_6 + LiAlH_4$	91
SiH_3Br	$PhSiCl_3 + LiAlH_4$, then HBr	92
SiH_3Cl	$SiH_3Br + HgCl_2$	93
SiH_3I	$(SiH_3)_3N + HI$	94
SiH_3F	$(SiH_3)_3N + NH_4HF_2$	95
$(SiH_3)_3N$	$SiH_3Cl + NH_3$	96
SiD_3Br	$Br_2 + SiD_4$	97
SiD_3Cl	$SiD_3Br + HgCl_2$	-
SiH_2I_2	$SiH_4 + HI + AlI_3$	98
$Me_2N.SiH_3$	$Me_2NH + SiH_3Cl$	99
Si_2H_5Cl	$Si_2H_6 + BCl_3$	80
Si_2Cl_6	$Cl_2 + CaSi_2$	100
GeH_4 and Ge_2H_6	$GeO_2 + BH_4^-$	101
GeH_3Br and GeH_2Br_2	$GeH_4 + HBr + AlBr_3$	102
GeH_3Cl	$GeH_3Br + HgCl_2$	-
GeH_3I	$GeH_3Cl + HI$	103
GeH_2Cl_2	$GeH_2Br_2 + HgCl_2$	-
Ge_2H_5Cl	$Ge_2H_6 + AgCl$	82
PH_3	heat H_3PO_3	104
PEt_3	$PCl_3 + EtMgBr$	105

Compound	Method	Reference
cis and trans-$(PEt_3)_2PtCl_2$	$K_2PtCl_4 + Et_3P$	106
trans-$(PEt_3)_2PtI_2$	NaI + trans-$(PEt_3)_2PtCl_2$	-
trans-$ClPt(PEt_3)_2H$	N_2H_4 + cis-$(PEt_3)_2PtCl_2$	52
trans-$XPt(PEt_3)_2H$	NX + trans-$ClPt(PEt_3)_2H$	52
trans-$(PEt_3)_2PdCl_2$	$K_2PdCl_4 + Et_3P$	107

The following materials were prepared by methods which differed slightly from those reported:

trans-$ClPt(PEt_3)_2D$[52]

Hydrazine hydrate (0.3 mls) in D_2O (15 mls) was added to cis-$(PEt_3)_2PtCl_2$ (1 gm) and heated at 100° for one hour in a sealed tube. The product was filtered off and recrystallised from 30/40 pet. ether. Yield = 0.75 gm. The infrared spectrum of the product showed trans-$ClPt(PEt_3)_2D$ with a little trans-$ClPt(PEt_3)H$ (~10%).

$SiH_3.SiHCl_2$[80]

Disilane (3 mmoles) was treated with BCl_3 (1.5 mmoles) for 10 hours at 0° in a reaction vessel of volume 100 mls. SiH_3SiHCl_2 was obtained pure (infrared and n.m.r.) by distilling once through a trap held at -45° and condensing five times in a trap held at -78°.

$SiH_2Cl.SiH_2Cl$[80]

Disilane (3 mmoles) was treated with BCl_3 (3mmoles) for $3\frac{1}{2}$ hours at 0° in a reaction vessel of volume 50 mls. The products were fractionated as described above for $SiH_3.SiHCl_2$ and the fraction held at -78° was $SiH_2Cl.SiH_2Cl$ with a little (5%) $SiH_3.SiHCl_2$ (infrared and n.m.r.)

Other compounds used were commercially available. The purity of the starting materials was checked spectroscopically and by measurement of vapour pressure for volatile compounds, boiling point for involatile liquids and melting point for solids.

Solvents were purified as follows:

Benzene	-	Analar grade, dried over sodium wire.
Toluene	-	As for benzene
T.M.S.	-	Distilled from a trap at -78°.
Deuterobenzene	-	Distilled and found adequately pure.
Monoglyme	-	Shaken with K/anthracene and distilled.
Diethyl ether	-	Sodium wire then distilled.
Diglyme	-	As for monoglyme.
Di-n-amyl ether	-	$LiAlH_4$, then distilled.

The range of solvents which were used for the silyl and germyl derivatives of platinum was very limited. Only benzene, toluene, deuterobenzene and tetramethylsilane were found to be inert. Chloroform, carbon tetrachloride, monoglyme, diethyl ether and acetone caused decomposition or reacted. The solvents were degassed on a vacuum line and stored in greaseless tap ampoules.

7.3 Preparations

Expt. 1.1. trans-$ClPt(PEt_3)_2SiH_2Cl$

In a typical experiment silyl chloride (0.295 mmole) was allowed to react with trans-$ClPt(PEt_3)_2H$ (0.295 mmole) in benzene (ca. 1 ml) at room temperature for five minutes. Hydrogen (0.290 mmole) was evolved and on evaporation of the solvent trans-$ClPt(PEt_3)_2SiH_2Cl$ was obtained as a white crystalline solid. (Found C, 25.6; H, 6.02; Cl, 13.6; P, 11.9%. $C_{12}H_{32}Cl_2P_2PtSi$ requires C, 27.1; H, 6.1; Cl, 13.3; P, 11.6%)

Expts. 1.2 - 1.6. trans-$BrPt(PEt_3)_2SiH_2Br$, trans-$IPt(PEt_3)_2SiH_2I$, trans-$ClPt(PEt_3)_2SiHCl_2$, trans-$IPt(PEt_3)_2SiHCl_2$, trans-$IPt(PEt_3)_2SiHI_2$.

These compounds were prepared as in Expt. 1.1. In each case the volume of hydrogen evolved was within 0.9 - 1.0 mole per mole of silyl compound taken as shown in Table 7.1 and the products were identified by their n.m.r. spectra. (For trans-$ClPt(PEt_3)_2SiHCl_2$, found: C, 26.1; H, 5.63; Cl, 17.6; P, 10.7%. $C_{12}H_{31}Cl_3P_2PtSi$ requires: C, 25.4; H, 5.5; Cl, 18.8; P, 10.9%).

Expt. 1.7. trans-$ClPt(PEt_3)_2SiH_2F$.

Silyl fluoride (0.247 mmole) was allowed to react with trans-$ClPt(PEt_3)_2H$ (0.247 mmole) in toluene at low temperatures. Hydrogen (0.23 mmole) was evolved at -40° and the product identified by its n.m.r. spectrum as trans-$ClPt(PEt_3)_2SiH_2F$. It decomposed in solution above -30° .

Expt. 1.8. trans-$ClPt(PEt_3)_2GeH_2Cl$.

Treatment of trans-$ClPt(PEt_3)_2H$ (0.172 mmole) with GeH_3Cl (0.172 mmole) at room temperature in benzene solution for five minutes gave hydrogen (0.168 mmole) and, on slow evaporation of the solvent at -22°, a pale yellow solid trans-$ClPt(PEt_3)_2GeH_2Cl$, identified by its n.m.r. spectrum. (Found: C, 24.9; H, 5.35%. $C_{12}H_{32}Cl_2GeP_2Pt$ requires: C, 24.98; H, 5.59%).

Expts. 1.9 - 1.11. trans-$BrPt(PEt_3)_2GeH_2Br$, trans-$IPt(PEt_3)_2GeH_2I$, trans-$ClPt(PEt_3)_2GeHCl_2$.

These compounds were prepared in solution as in Expt. 1.8, and were identified by hydrogen evolution (as shown in Table 7.1) and by their n.m.r. spectra. The solutions decomposed as the solvents were evaporated.

Table 7.1

The amount of hydrogen (mmoles) evolved in a reaction between x mmoles of MH_3X and y mmoles of trans-$YPt(PEt_3)_2H$.

MH_3X	x	Y	y	H_2
SiH_3Cl	0.295	Cl	0.295	0.290
SiH_3Br	0.198	Br	0.198	0.187
SiH_3I	0.229	I	0.229	0.218
SiH_2Cl_2	0.246	Cl	0.246	0.236
GeH_3Cl	0.172	Cl	0.172	0.168
GeH_3Br	0.193	Br	0.193	0.184
GeH_3I	0.210	I	0.210	0.191

Expt. 1.12. trans-$ClPt(PEt_3)_2SiCl_3$.

Trichlorosilane (0.075 mmole) was reacted with trans-$ClPt(PEt_3)_2H$ (0.075 mmole) for one day. The reaction was not quite complete as only 0.064 mmole of H_2 was evolved. The product was identified as trans-$ClPt(PEt_3)_2SiCl_3$ by an infrared spectrum (c.f. ref. 30).

Expt. 1.13. trans-$ClPt(PEt_3)_2SiH_3$.

Monosilane and trans-$ClPt(PEt_3)_2H$ were allowed to react in equimolar proportions in benzene solution at room temperature. Hydrogen was evolved slowly, corresponding in a series of experiments to 0.7 to 0.95 mole per mole of starting material over one week. In one experiment SiH_4 (0.342 mmole) was treated with trans-$ClPt(PEt_3)_2H$ (0.342 mmole) and the amount of hydrogen evolved was investigated with the time of reaction:

Table 7.2

time (hours)	1	20	30	50	80
H_2 (total mmoles)x10	0.03	0.48	1.49	2.29	2.92

The solution turned yellow after 30 hours and after 80 hours the experiment was discontinued because the solution was dark brown. The product $ClPt(PEt_3)_2SiH_3$ was identified in another experiment, in toluene solution at 0°, but it could not be isolated as a solid because only a brown tar remained after evaporation of the solvent.

Expt. 1.14. trans-$BrPt(PEt_3)_2SiH_3$.

Monosilane (0.271 mmole) and trans-$BrPt(PEt_3)_2H$ (0.271 mmole) in benzene over two days gave hydrogen (0.273 mmole) and trans-$BrPt(PEt_3)_2SiH_3$, identified by its n.m.r. spectrum and isolated as a pale yellow solid by evaporation of the solvent. (Found: C, 26.8; H, 5.6; Br, 13.9; P, 10.8%. $C_{12}H_{33}BrP_2PtSi$ requires: C, 26.6; H, 6.1; Br, 14.7; P, 11.4%).

Expt. 1.15. trans-$IPt(PEt_3)_2SiH_3$.

Monosilane (0.271 mmole) reacted in benzene over two days with trans-$IPt(PEt_3)_2H$ (0.271 mmole) to give hydrogen (0.26 mmole) and trans-$IPt(PEt_3)_2SiH_3$. (Found: C, 24.45; H, 5.4%. $C_{12}H_{33}IP_2PtSi$ requires: C, 24.45; H, 5.6%).

Expts. 1.16 - 1.21. trans-$BrPt(PEt_3)_2SiH_2Cl$, trans-$IPt(PEt_3)_2SiH_2Cl$, trans-$IPt(PEt_3)_2SiH_2Br$.

These compounds, which were prepared as in Expt. 1.1, were identified by the volume of hydrogen evolved in the preparative reaction and by their n.m.r. spectra. The same n.m.r. spectra were obtained from the products of reaction of SiH_3Cl with trans-$BrPt(PEt_3)_2H$ and of SiH_3Br with trans-

$ClPt(PEt_3)_2H$; from SiH_3Cl with trans-$IPt(PEt_3)_2H$ and from SiH_3I with trans-$ClPt(PEt_3)_2H$; from SiH_3Br with trans-$IPt(PEt_3)_2H$ and from SiH_3I with trans-$BrPt(PEt_3)_2H$. The compounds were isolated as solids by evaporation of solvent.

Expts. 1.22 - 1.27. trans-$BrPt(PEt_3)_2GeH_2Cl$, trans-$IPt(PEt_3)_2GeH_2Cl$, trans-$IPt(PEt_3)_2GeH_2Br$.

These compounds were identified by their n.m.r. spectra and by the volume of hydrogen evolved; they were each prepared in two ways in reactions analogous to Expts. 1.16 - 1.21. The compounds decomposed on evaporation of solvent.

Expt. 2.1. $I_2Pt(PEt_3)_2H.SiH_2I$.

Trans-$IPt(PEt_3)_2SiH_2I$ (0.200 mmole), prepared as in Expt. 1.3 in benzene solution was treated with hydrogen iodide (0.400 mmole) at 0° for 5 minutes. The solvent was evaporated at -22° and the fraction which was volatile at -96° was collected in a tube containing $AgNO_3$ solution and yielded 0.194 mmole AgI. The yellow crystalline solid remaining was $I_2Pt(PEt_3)_2H.SiH_2I$ (Found: C, 17.10; H, 3.86%. $C_{12}H_{33}I_3P_2PtSi$ requires: C, 17.09; H, 3.94%).

Expt. 4.1. trans-$ClPt(PEt_3)_2Ge_2H_5$.

Digermane (0.201 mmole) was reacted with trans-$ClPt(PEt_3)_2H$ (0.201 mmole) at 0° in benzene for five minutes; hydrogen (0.199 mmole) was evolved and trans-$ClPt(PEt_3)_2Ge_2H_5$ was formed. The product was identified by its n.m.r. spectrum. It decomposed completely (no n.m.r. signal in the Ge<u>H</u> region) after 15 minutes at room temperature giving a dark brown solution.

7.4 Reactions

Expt. 2.2 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with HCl.

A benzene solution of trans-$ClPt(PEt_3)_2SiH_2Cl$ (0.261 mmole) was treated with HCl (0.261 mmole) for 15 minutes at room temperature. Hydrogen (0.259 mmole) was evolved and the other product was identified by its n.m.r. spectrum as trans-$ClPt(PEt_3)_2SiHCl_2$.

Expt. 2.3 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with 2HCl.

A benzene solution of trans-$ClPt(PEt_3)_2SiH_2Cl$(I) (0.125 mmole) was allowed to react with HCl (0.250 mmole) for two days at room temperature; hydrogen (0.22 mmole) was evolved, and the residue after evaporation of the solvent was identified by its infrared spectrum as trans-$ClPt(PEt_3)_2SiCl_3$.

Expt. 2.4 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with 3HCl.

Treatment of a solution of (I) (0.115 mmole) in benzene with HCl (0.345 mmole) at room temperature gave hydrogen (0.21 mmole) and trans-$ClPt(PEt_3)_2SiCl_3$. The product was identified by its infrared spectrum. No $HSiCl_3$ or $SiCl_4$ was evolved even after heating the mixture to 100° for several hours.

Expt. 3.1 Reaction of solid trans-$ClPt(PEt_3)_2SiH_2Cl$ with liquid hydrogen chloride.

Hydrogen chloride (0.585 mmole) was repeatedly condensed onto solid (I) (0.195 mmole) and allowed to warm to room temperature. $SiHCl_3$ (0.076 mmole) was evolved leaving a mixture of trans-$ClPt(PEt_3)_2SiCl_3$ and $Cl_2Pt(PEt_3)_2H_2$. The products were identified by their nujolmull infrared spectra. The compound $Cl_2Pt(PEt_3)_2H_2$ has a characteristic, strong infrared peak at 2254 cm^{-1} with a shoulder at 2265 cm^{-1} [52].

Expt. 3.2 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with methanol.

In a series of experiments, methanol was added to equimolar quantities of (I) in benzene at room temperature. Hydrogen was evolved rapidly in amounts varying from 0.65 to 1.0 mole per mole of (I) taken. The other volatile products were distilled through a trap held at -78° to remove benzene. The fraction passing through -78° was further distilled through a trap held at -96°. The infrared spectrum of the fraction which passed through -96° indicated traces of SiH_4 and SiH_2Cl_2 and other peaks at: 2960m, 2840 w, 2230 s, 1460 w, 1195 w, 1110 s, 902 v.s, 640 m, 540 s cm^{-1}. By comparison with the infrared spectra of CH_3OSiH_3 [108] and $(MeO)SiHCl_2$ [74], the peaks were tentatively assigned to the compound $(MeO)SiH_2Cl$. This fraction was condensed with

benzene as solvent into an n.m.r. tube, and the resulting spectrum indicated a mixture of silanes and methoxysilanes probably SiH_4, SiH_2Cl_2, $(MeO)_3SiH$, $MeOSiHCl_2$ and $MeOSiH_2Cl$. The n.m.r. parameters of the methoxysilanes have been listed in Table 3.1; they may have been formed by disproportionation of $MeOSiH_2Cl$ in solution. The fraction condensing in -96° was probably $(MeO)_2SiHCl$, as it had an infrared spectrum exactly as reported for $(MeO)_2SiHCl$[74]. The n.m.r. spectrum of this fraction in benzene indicated only $(MeO)_3SiH$ and $MeOSiHCl_2$, again possibly due to disproportionation. The infrared and n.m.r. spectra of the involatile residue when dissolved in benzene indicated the presence of trans-$ClPt(PEt_3)_2H$ [ν(Pt-H) = 2180 cm^{-1}] and another compound possibly trans-$ClPt(PEt_3)_2SiHCl(OMe)$. The n.m.r. parameters are listed in Table 3.2. Some infrared frequencies with tentative assignments are shown below in Table 7.3.

Expt. 3.3 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with methanol in the presence of trimethylamine.

Methanol and trimethylamine were added in equimolar proportions to an equimolar quantity of (I) in toluene at -22°. A white solid was precipitated and was filtered off by decanting the solution through a sinter sealed into the reaction vessel. The n.m.r. spectrum of the solution was consistent with trans-

$ClPt(PEt_3)_2SiH_2(OMe)$ and the parameters have been listed in Table 3.2. The infrared spectrum was different from that assigned to trans-$ClPt(PEt_3)_2SiHCl(OMe)$ and is shown with tentative assignment of some bands in Table 7.1.

Table 7.3

tentative assignment of bands.

possible compound	ν(SiH)	ν(SiO)	ν(SiCl)	δ(SiH) cm^{-1}
$ClPt(PEt_3)_2SiHCl(OMe)$	2095	1070	490	885
$ClPt(PEt_3)_2SiH_2(OMe)$	2040	1060	-	900

The infrared spectrum of the solid filtered off at the sinter was consistent with its formulation as $Me_3NH^+Cl^-$.

Expt. 3.4 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with water.

Water (0.233 mmole) reacted rapidly with (I) (0.233 mmole) in benzene at room temperature; hydrogen (0.233 mmole) was evolved leaving a white solid residue which was insoluble in common solvents and gave no well-defined infrared bands. Evaporation of benzene from the liquid gave $Cl_2Pt(PEt_3)_2H_2$ (identified by ν(PtH) = 2154 s, 2165 sh).

Expt. 3.5 Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with dimethylamine.

Me_2NH (0.410 mmole) was added slowly with shaking to a solution in toluene of (I) (0.205 mmole). The toluene and

Me_2NH were maintained at -22°. A white solid was precipitated and the solution was filtered through a sintered disc. Evaporation of the solvent at -22° gave trans-$ClPt(PEt_3)_2SiH_2NMe_2$ a pale brown sticky paste, identified by its n.m.r. spectrum (Table 3.2), infrared spectrum [ν(SiH) = 2040, 2060; δ(SiH) = 870 cm^{-1}] and analysis. (Found: C, 30.8; H, 6.8%. $C_{14}H_{38}ClNP_2PtSi$ requires C, 31.1; H, 7.1%).

Expt. 3.6. Reaction of trans-$ClPt(PEt_3)_2SiH_2NMe_2$ with methyl iodide.

Trans-$ClPt(PEt_3)_2SiH_2NMe_2$ prepared as in Expt. 3.5 was treated with an equimolar amount of MeI in toluene solution at -22°. A white solid was slowly precipitated. After one week the solution began to turn pale brown and was then filtered off through a sintered disc. An attempt was made to take an infrared spectrum of the white solid, but it decomposed to a brown tar on warming to room temperature. The solid may have been [trans-$ClPt(PEt_3)_2SiH_2NMe_3]^+I^-$.

Expt. 3.7. Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with triethylphosphine.

Addition of Et_3P in equimolar amounts to a solution of (I) in benzene led to collapse of J(HSiPtP) at temperatures

down to -30°. No further evidence of any reaction was detected. Evaporation of the solvent led to decomposition. Addition of Et_3P to solid(I) also led to decomposition.

Expt. 3.8. Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with phosphine.

Treatment of (I) in benzene solution with a molar excess of PH_3 at room temperature led initially to no change in the n.m.r. spectrum of (I). Over a period of days at room temperature, small amounts of white solid precipitated and J(HSiPtP) collapsed. An attempt was made to identify the white solid by infrared spectroscopy, after decanting off the solution, however it changed into a sticky brown tar with no well-defined infrared bands.

Expts. 3.9 - 3.11. Reaction of trans-$ClPt(PEt_3)_2SiH_2Cl$ with ethylene, cyclohexene and phenylacetylene.

Solutions of (I) in benzene were treated with equimolar amounts of C_2H_4, C_6H_{10} and $Ph.C_2H$. The n.m.r. spectra showed no sign of any reaction but for C_2H_4 the HSi resonance was broad and J(HSiPtP) was not observed.

Expt. 3.12 Reaction of $I_2Pt(PEt_3)_2H.SiH_2I$ with triethylphosphine.

A solution of $I_2Pt(PEt_3)_2H.SiH_2I$ in benzene at 0° was treated with an equimolar amount of Et_3P, and there was

immediate precipitation of a pale yellow solid. The solution was decanted off and identified spectroscopically (n.m.r. and infrared) as containing trans-$IPt(PEt_3)_2SiH_2I$. The infrared spectrum of the solid was consistent with $Et_3PH^+I^-$.

Expt. 3.13. Reaction of excess SiH_3Cl with trans-$ClPt(PEt_3)_2SiH_2Cl$.

Addition of silyl chloride to a solution of an equimolar amount of (I) in benzene led initially to no change in the n.m.r. spectrum of (I). After periods of time at room temperature ranging from hours to days, the n.m.r. peaks broadened and those due to SiH eventually collapsed, while the solution separated into two phases. The infrared spectrum of each phase indicated the presence of SiH (ν(SiH)~2000 cm^{-1}) but neither phase gave well-defined n.m.r. spectra. Evaporation of benzene from the lower phase led to formation of a sticky gel. In a typical experiment SiH_3Cl (0.314 mmole) was treated with trans-$ClPt(PEt_3)_2H$ (0.157 mmole) for two weeks and hydrogen (0.35 mmole) was evolved.

Expt. 5.1 Reaction of trans-$ClPt(PEt_3)_2H$ with a threefold excess of germyl chloride.

Trans-$ClPt(PEt_3)_2H$ (0.235 mmole) was treated with GeH_3Cl (0.705 mmole) for ten minutes at room temperature

in benzene. Hydrogen (O. 357 mmole) was evolved, together with HCl (O. O32 mmole) and unreacted GeH_3Cl (O. O85 mmole). The n.m.r. spectrum of a similar reaction has been shown in Figure 5.1 and has been interpretated in terms of the formation of some tris-(germyl)-platinum compounds. The amount of GeH_3Cl used is consistent with such a reaction.

Expt. 5.2. Reaction between trans-$IPt(PEt_3)_2H$ and a two-fold excess of GeH_3I.

Trans-$IPt(PEt_3)_2H$ (O. 133 mmole) was reacted with GeH_3I (O. 266 mmole) in benzene. Hydrogen was evolved and a pale yellow solid was precipitated. The n.m.r. spectrum of the dilute solution indicated the presence of unreacted GeH_3I, some trans-$IPt(PEt_3)_2GeH_2I$ and another compound with n.m.r. parameters: τ = 5.95 p.p.m., J(HGePtP) = 6 Hz and J(HGePt) = 67.5 Hz. On evaporation of the solvent the infrared spectrum indicated a platinum-hydrogen stretch: ν(PtH) = 2198 cm^{-1}, as well as germanium-hydrogen stretches at 1980 cm^{-1} and 2000 cm^{-1}. These results are consistent with the possible formation of a hydride compound of six-coordinated platinum, perhaps $IPt(PEt_3)_2H.(GeH_2I)_2$.

All the other experiments were carried out in n.m.r. tubes, and the course of each reaction was followed by the n.m.r. spectrum. The results of these experiments have been discussed in Chapters I - V.

APPENDIX

THE PRODUCTS OF BASE CATALYSED DISPROPORTIONATION OF HEXACHLORODISILANE.

Introduction

While engaged in a study of the formation of adducts between trimethylamine and hexachlorodisilane, Urry and his co-workers "stumbled" across a convenient method for the preparation of perchloropolysilanes[109]. They claimed that hexasilicon tetradecachloride was produced by base catalysed disproportionation of Si_2Cl_6:

$$5Si_2Cl_6 \xrightarrow{Me_3N} Si_6Cl_{14}.SiCl_4 + 3SiCl_4$$

Wiberg repeated the reaction and claimed, from a determination of the stoichiometry, that the product was Si_5Cl_{12}[110]:

$$4Si_2Cl_6 \longrightarrow Si_5Cl_{12} + 3SiCl_4.$$

This discrepancy in the interpretation of the nature of the products was apparently resolved by Urry in a later series of papers. The formation of Si_5Cl_{12} or Si_6Cl_{14} seemed to depend on the conditions of the reactions.

Pentasilicon dodecachloride was formed either by using a large amount of the catalyst Me_3N,[111] or by allowing any $SiCl_4$ produced in the disproportionation to be removed as soon as it was formed[112]. The compound Si_5Cl_{12} was produced

as white, needle-like crystals which formed an adduct with $SiCl_4$.

Hexasilicon tetradecachloride was formed when $SiCl_4$, produced by the disproportionation of Si_2Cl_6, was allowed to accumulate in the reaction mixture[113]. Under these conditions the $SiCl_4$ adduct of Si_6Cl_{14} was formed as clear cubic crystals. Removal of $SiCl_4$ in vacuo at room temperature led to formation of Si_6Cl_{14} as a white microcrystalline solid which was shown to exhibit polymorphism. It was shown to occur in at least four forms, which could be interconverted by various paths.

Both the compounds Si_5Cl_{12} and Si_6Cl_{14} were identified by analysis and by molecular weight determinations. The methods used for determining the molecular weight were: elevation of boiling point (in CH_2Cl_2 solution), isopiestic measurements (in CH_2Cl_2) and vapour pressure of a known weight at a known temperature in a calibrated volume.

On the basis of a study of the infrared spectra in the vapour phase and in CH_2Cl_2 solution[114], a neopentyl-type structure was assigned to Si_5Cl_{12} and a neo-hexyl-type structure to Si_6Cl_{14}. The conclusions reached by Urry must be regarded as tentative, however, because a rigorous assignment of all the infrared bands was not made. The amount of definative data obtainable from these compounds was limited because of the handling difficulties. In common with most chlorides of silicon Si_5Cl_{12} and Si_6Cl_{14} were extremely moisture-sensitive, and the

range of usable inert solvents was very small. The compounds were only slightly volatile and high temperature gas cells were designed in order to record the vapour phase spectra. It seemed that a more reliable indication of the structures could be provided by an X-ray study of the compounds.

Results and Discussion

The compounds Si_5Cl_{12} and Si_6Cl_{14} were prepared exactly as described by Urry[112, 113]. The infrared spectra of nujol mulls of the compounds agree very closely with the results obtained by Urry except that the band at 536 cm^{-1}, which he assigned to the symmetrical Si-Cl stretch, is missing from the spectra of both compounds; thus the spectra are identical in the range studied (800 - 400 cm^{-1}). The Raman spectra also show no difference between the two compounds. The frequencies of the Raman bands are shown together with those from the infrared spectra in Table A.1.

The identity of the Raman and infrared spectra of Si_5Cl_{12} and Si_6Cl_{14} suggested that Urry's formulation of these compounds was incorrect. They are more likely to be different forms of the same compound, either Si_5Cl_{12} or Si_6Cl_{14}, consistent with the known polymorphism of Si_6Cl_{14}. The X-ray powder photographs of Si_5Cl_{12} and Si_6Cl_{14} are identical[115] and the crystal structure of the clear cubic crystals thought to be

Table A.1

Vibrational frequencies of Si_5Cl_{12} and (Si_6Cl_{14}) measured in cm^{-1}.

Compound	Conditions	Vibrational frequencies.					
Si_5Cl_{12} [a]	vapour	590 s	555 w	396 m			
(Si_6Cl_{14}) [a]	vapour	595 s	555 w	536 w	396 m		
Si_5Cl_{12} [a]	CH_2Cl_2 soln.	595 s	555 w	536 w	400 m		
(Si_6Cl_{14}) [a]	CH_2Cl_2 soln.	595 s	555 w	536 w	400 m		
Si_5Cl_{12}	nuj. mull	600 s	557 w				
(Si_6Cl_{14})	nuj. mull	600 s	558 w				
Si_5Cl_{12} [b]	solid	608 w, 586 w	559 m			311 vs	183 s 116 s
(Si_6Cl_{14}) [b]	solid	608 w, 586 w	559 m			311 vs	183 s 116 s

(a) determined by Urry[114].

(b) Raman frequencies; the other frequencies are from infrared spectra.

$Si_6Cl_{14}.SiCl_4$ has been determined by X-ray diffraction[117]; the correct formulation is $Si_5Cl_{12}.SiCl_4$.

Conclusion

There is no definite evidence to suggest that the compounds prepared in this work were the same as those prepared by Urry but it seems most probable that they were. The preparative methods of Urry were followed exactly and the appearance of the resulting products fitted his description. Thus the two compounds originally thought to be Si_5Cl_{12} and Si_6Cl_{14} are probably both Si_5Cl_{12}, possibly different crystalline forms. Only a small error in Urry's analytical data would explain the discrepancy but his molecular weight determinations by the rather unreliable methods that he used must have been incorrect.

Experimental

Hexachlorodisilane was prepared from Cl_2 and $CaSi_2$[100] and Si_5Cl_{12} and (Si_6Cl_{14}) were prepared exactly as described by Urry[112, 113]. The compounds were handled under dry nitrogen in a polythene bag. Infrared spectra were recorded on a Perkin-Elmer KBr infracord and Raman spectra were recorded, using finely ground solid samples, on a Cary 81 laser Raman spectrometer.

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